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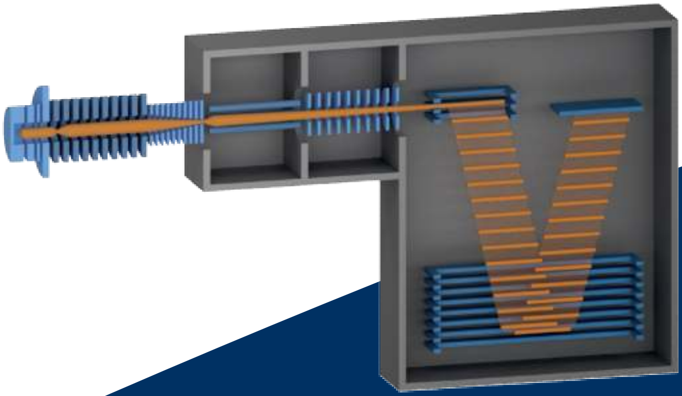

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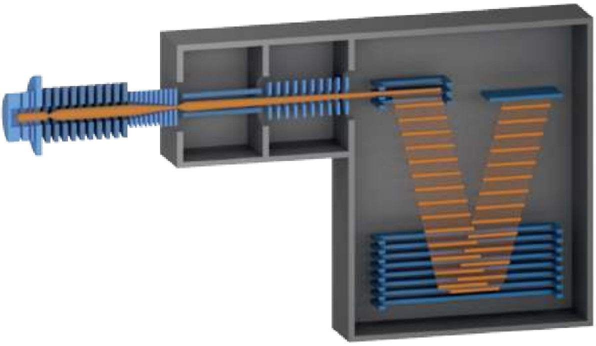

Contributions

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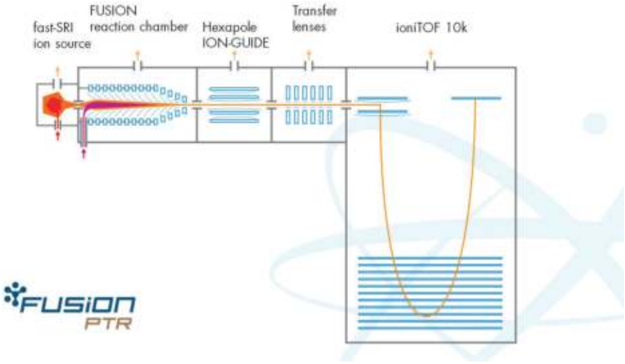
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Foreword

In the 1990's proton transfer reaction mass spectrometry (PTR-MS) using H_3O^+ reagent ions became a widely used analytical instrument with applications in Environmental Science, Medical Applications and Food Technology due to the large amount of volatile organic compounds (VOC), which can be quantitatively ionized. In 1998 the spin-off company Ionicon Analytik GmbH (www.ionicon.com) was founded to provide PTR-MS instruments to a growing user community and to develop the technology further. Today many research institutions and companies use this technology throughout the world.

The intent in initiating and organizing the 1st International PTR-MS Conference in January 2003 in Igls, Austria was to bring together active scientists and technology experts involved in mass spectrometric measurements of VOC. More than 20 years later after a short break due to the Corona pandemic we continue this series with the 9th PTR-MS conference, providing a discussion forum for PTR-MS users and scientists from both academia and industry. This year's conference takes place from January 26th to 29th in the Conference Centre of Seefeld, a small village close to Innsbruck, Austria.

The conference topics of this year conference are Environmental Science, Food & Flavour Science, Health Science and Instruments / Technology and Future Trends. I would like to thank the session chairs Karena McKinney from Colby College, USA (Environmental Science), Franco Biasioli from FEM, Italy (Food & Flavour Science), Jonathan Beauchamp from Fraunhofer IVV, Germany (Health Science) and Jens Herbig from Ionicon Analytik, Austria (Industrial Applications) for putting together an exciting programme, which exemplifies the growing number of PTR-MS users in various scientific disciplines and industrial applications.

Special thanks go to Jürgen Dunkl and Gertrud Sommeregger, who helped organizing this exciting conference. Finally, I would like to thank the UNIVERSITY of INNSBRUCK and IONICON ANALYTIK sponsoring the conference.

Armin Hansel

Innsbruck, January 2024

Applications in Environmental Science

Rapid on-site detection of Acer infested by Anoplophora glabripennis (Motschulsky) by fastGC–PTR–TOF

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Abstract

Invasive species and their prevention and control is becoming increasingly important. Herein, the potential of a mobile fastGC–PTR–TOF for the detection of invasive species at an early stage is shown exemplarily for the Asian Longhorned Beetle (ALB). Without the need of pre-concentration, volatiles associated with an ALB infestation could be identified within less than two minutes.

Introduction

The number of invasive species and their impact on the local ecosystem is increasing dramatically, favored by globalization and climate change. The report on invasive alien species by Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services (IPBES) emphasizes the need of effective management to eradicate or, at least, to contain further spread of invasive species [1]. Anoplophora glabripennis (Motschulsky), known as Asian Longhorned Beetle, is an invasive species originating from East Asia. It causes enormous actual and potential damage in many parts of the world, including Europe, because ALB is a polyphagous wood-boring beetle with a large list of possible host trees [2]. If the presence of ALB is confirmed, a demarcated area with a radius of at least 2 km must be monitored intensively for at least four consecutive years. Current monitoring techniques cover visual control, pheromone traps and sniffer dogs. In case of visual control experts look for external signs such as exit holes, oviposition pits, frass and exposed feeding tunneling. The detection rate of standing trees ranges from 20–36%, which is even worse for recently infested trees [3]. Efficiency can be improved by using mobile elevated platforms or tree climbers. Pheromone traps are the method of choice for several flying insects, but in case of ALB they have not reached operational efficacy to date [4]. Sometimes, these methods are complemented by sniffer dogs, which show remarkable sensitivities (75–88%) and specificities (85–96%) for the detection of ALB frass in test scenarios [5].

However, there is no currently available mobile and fast instrumental analytical technique for the detection of ALB by its emitted volatile organic compounds (VOC) so far. Extensive research on the volatiles emitted by different stages of ALB was done by Makarow et al. using thermal desorption gas chromatography mass spectrometry (TD–GC/MS) [6]. Among over 200 emitted VOCs, five volatiles were mentioned, that give a very strong hint to an ALB-infestation, namely the three sesquiterpenes (+)-cyclosativene, α-longipinene, copaene/α-cubebene, the monoterpene 3-carene and the hydrocarbon 2,4-dimethyl-heptene [7]. These results are used in this study to develop an early-stage detection method based on the highly sensitive and mobile PTR–TOF, allowing for the online-detection of VOCs in the ppb–ppt range. As the target compounds belong to the group of terpenes with several thousand of isomers, the PTR–TOF is equipped with a fastGC add-on, which enables a short pre-separation prior to the actual analysis.

Experimental Methods

Instrument

All experiments were conducted with a compact and mobile PTR–TOF 1000 (IONICON Analytik GmbH, AT) using H_3O^+ as reagent ion. The device was equipped with a commercial fastGC add-on (IONICON Analytik GmbH, AT) [8]. The optimal ionization conditions were evaluated by varying the reduced field (E/N) from 140–60 Td in steps of 10 Td by applying different drift tube voltages. The following instrument parameters were used: (a) PTR drift tube: p_{drift} 2.5 mbar, T_{drift} 100 °C, U_{drift} 360 V, resulting in E/N of 80 Td. (b) Nitrogen 5.0 carrier gas flow of 8 mL min^{-1}, (c) a non-polar MXT–1 column (10 m, 0.53 mm I.D., 1 µm df, Restek, Bellefonte, PA), (d) injection time 80 s, measuring time 100 s, temperature ramp consisted of 10 s at 45 °C, heat to 100 °C at 5.5 °C s^{-1}, then to 110 °C at 0.5 °C s^{-1}, followed by heat to 165 °C at 2.75 °C s^{-1}, held for 10 s. Mass spectra were acquired at a scan speed of 0.1 s in the mass range m/z 0-277. PTR–TOF data were evaluated with the PTR-MS Viewer 3.4.5, followed by OriginPro 2021b.

As reference, TD–GC/MS measurements were carried out in parallel and analyzed as described by Makarow et al. with a GC-MS QP 2020 (Shimadzu) coupled to an OPTIC-4 multimode inlet. TD–GC/MS data were analyzed with GCMSsolution 4.41.

Samples and sampling procedure

Measurements were taken of a maple tree (Acer freemanii autumn blaze), recently infested by ALB, and of a stressed, but non-infested maple tree (Acer saccharinum), both growing indoors. The infested maple tree was measured in the in-house quarantine breed station at the Hochschule Bonn-Rhein-Sieg (HBRS). ALB larvae, originating from the Animal and Plant Health Inspection Service (APHIS) of the United States Department of Agriculture (USDA), were allowed to reproduce in the in-house quarantine breed station, equipped with living maple trees. Emissions of the maple trees were analyzed directly at the tree trunk. According to Makarow et al. [6] 10–20 cm of the trunk was wrapped with Nalophan® foil, closed by staples and fixed by foam padded lashing straps. To avoid particles from entering the device, the air from inside the foil is pumped through a PTFE syringe filter (5 µm), that is connected airtight to the foil and to the heated PEEK inlet capillary (100 °C) of the PTR–TOF. For TD–GC/MS measurements, volatiles were enriched on Tenax® TA for 90 min with a flow of 30 mL/min using a mobile air pump (Gilian GilAir Plus).

Results and Discussion

Ionization conditions

First, the VOCs emitted by the maple tree trunk upon infestation with ALB were measured in the direct mode in order to optimize the ionization conditions regarding the sensitivity of the protonated molecular ion of the target compounds. It should be noted that the primary ion distribution and thus the ionization conditions in the fastGC mode slightly differ from those in the direct inlet mode. The lack of humidity in the gas supply during fast GC runs results in H_3O^+ being the predominant primary ion at 80 Td, while in the direct mode the water dimer $H_2O{\cdot}H_3O^+$ is predominant.

fastGC

The observed masses in the fastGC–PTR–TOF measurements could be divided into compounds deriving from surrounding air, like oxygen (m/z 31.99 O_2^+) and humidity (m/z 39.03 ^{18}O water dimer), protonated molecular ions $[M+H]^+$ and fragments. In the following only the mass traces of protonated molecular ions are discussed and shown in Figure 1. The most intense peak was acetone at m/z 59.05, which is not shown for reasons of clarity and because of its unspecific character.

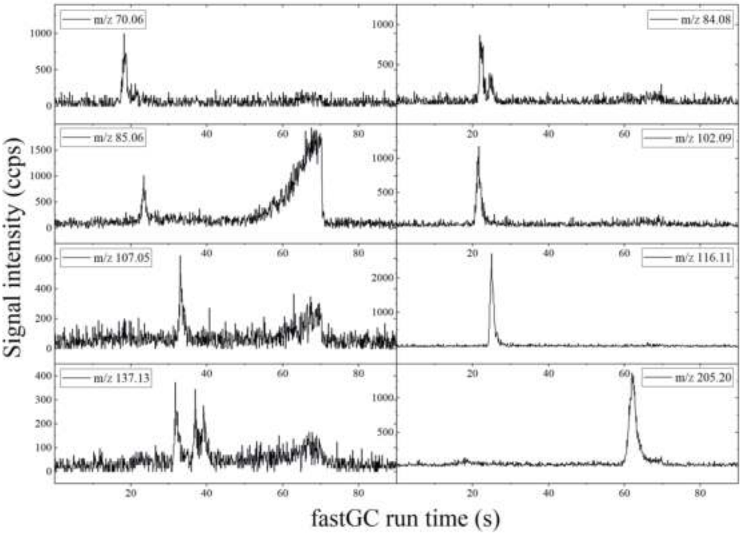

Figure 1: FastGC–PTR–TOF chromatograms of VOCs emitted by maple tree trunk upon infestation with ALB. Column: MXT-1. E/N = 80 Td. ccps = corrected counts per second.

Identification of the masses was done by generating sum formulas with the PTR–MS Viewer, resulting in an overall correctness of more than 90% for the suggested formulas (Table 1). The results were verified by identification of the peaks measured with TD–GC/MS, showing good agreement between both methods. The five most intense volatiles obtained by GC/MS correspond to the most intense masses measured with fastGC–PTR–TOF (m/z 102.09, m/z 116.11 and m/z 205.20), except for acetone, which is hardly adsorbed by Tenax® TA. Among these peaks, the sesquiterpenes with m/z 205.20 are of special interest. The three ALB-related sesquiterpenes (+)-cyclosativene, α-longipinene, (−)-α-copaene are detected in GC/MS, but appear as one broad peak in fastGC–PTR–TOF. Several approaches to enhance the resolution, like varying the temperature

Table 1 Substances found by fastGC–PTR–TOF, verified by TD-GC/MS, in the order of elution

	fastGC–PTR–TOF				TD–GC/MS			
#	t_R (s)	$[M+H]^+$	Sum formula	Correctness (%)	t_R (min)	Suggested compound	CAS	SI
1	13.9	59.05	C_3H_6O	92.18	1.402	Acetone	67-64-1	97
2	18.2	70.06	C_4H_7N	92.13	2.234	Isobutyronitrile	78-82-0	96
3	21.6	102.09	$C_5H_{11}NO$	92.04	3.067	1-Methoxy-2,3-dimethylaziridine	61593-25-7	81
4	21.9	84.08	C_5H_9N	91.70	3.679	2-Methylbutanenitrile	18936-17-9	96
5	24.4	85.06	C_5H_8O	90.76	4.123	2-Methyl-2-butenal	497-03-0	95
6	25.0	116.11	$C_6H_{13}NO$	92.10	4.943	(1Z)-2-Methylbutanal oxime	49805-56-3	84
7	31.7	137.13	$C_{10}H_{16}$	91.35	8.425	(+/−)-α-Pinene	80-56-8	97
8	33.0	107.05	C_7H_6O	92.79	8.934	Benzaldehyde	100-52-7	98
9	37.0	137.13	$C_{10}H_{16}$	91.35	10.084	3-Carene	13466-78-9	96
10	39.1	137.13	$C_{10}H_{16}$	91.35	10.802	cis-β-Ocimene	3338-55-4	98
11	62.0	205.20	$C_{15}H_{24}$	93.16	16.712	(+)-α-Longipinene	5989-08-2	97
12	62.0	205.20	$C_{15}H_{24}$	93.16	17.020	(+)-Cyclosativene	22469-52-9	95
13	62.0	205.20	$C_{15}H_{24}$	93.16	17.099	(−)-α-Copaene	3856-25-5	95

t_R = retention time, SI = similarity index of the spectrum of the detected peaks and library spectrum (NIST 14) program, the carrier gas (He), the gas flow velocity and using another type of capillary column (MXT–5) did not result in resolved peaks. The other two dominant masses with m/z 102.09 and m/z 116.11 could not be identified unequivocally by GC/MS (similarity index below 90). In this case, the high-resolution PTR-TOF gave additional information on probable sum formulas ($C_5H_{11}NO$ and $C_6H_{13}NO$, respectively), which correspond to the observed GC/MS mass spectra, but in case of $C_6H_{13}NO$ not to the suggested compounds by comparison with NIST. Furthermore, these substances have not been published in literature related to ALB and could be of interest in further studied. Besides, three monoterpene peaks were found by fastGC–PTR–TOF, which could be identified as α-pinene, 3-carene and cis-β-ocimene by GC/MS.

The origin of the measured emissions was verified by comparison with background measurements inside the quarantine station and with a stressed, but non-infested tree. In the quarantine station, 3-carene and α-pinene occurred in equal concentration as observed at the tree trunk. All the other VOCs were not present or in lower concentrations, indicating that they are emitted by the tree itself. The non-infested acer emitted α-pinene and benzaldehyde, but none of the other compounds.

To sum it up, the combination of fastGC with PTR–TOF was successfully used as a fast and mobile detection device for maple trees in an early stage of infestation with ALB. Further studies need to be carried out to achieve resolution of all target compounds, especially of the sesquiterpenes. Overall, it bears the potential to improve the effectiveness of monitoring methods against invasive wood-boring species, especially of recently infested trees, where visual control is often insufficient.

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Monitoring of volatile emission circadian rhythm in pests using PTR-ToF and GC-MS

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Abstract

Insects often exhibit diel (daily) rhythms in their behaviors, including their emissions of volatile organic compounds. These compounds play various roles in insect communication, defense, foraging, and reproduction. The emission of volatiles can vary throughout the day in response to environmental factors like light, temperature, and circadian rhythms. This diel rhythm in volatile emissions can have ecological implications, influencing interactions between insects and their environment. The relevance of these variations is however often underestimated, even if some compounds act like intraspecific messengers, according to their source and timing of release. Such compounds can have nonetheless important implications in the management of pest species, such as in control and detection. We present here a recent study in which the emission diel rhythm of the olive fruit fly *Bactrocera oleae* headspace was examined through the combination of Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-ToF) and Gas Chromatography coupled with Mass Spectrometry (GC-MS). This novel approach revealed sex and time specific emissions that were so far unreported due to limitations of commonly used analytical techniques. Expanding the application of this method to other insects will lead to a deeper understanding of their emissions and intraspecific communication. It can further contribute to the development of innovative pest-detection techniques based on signature volatiles, and it will be tested on the brown marmorated stink bug *Halyomorpha halys* within the PURPEST project.

Urban enhancement ratios over North America during the AEROMMA campaign

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Abstract

We present comprehensive urban enhancement ratios (ERs) for volatile organic compounds (VOCs) and oxygenated VOCs (OVOCs) observed during the AEROMMA campaign [1]. Flights aboard the NASA DC-8 were conducted over various locations in North America, including Los Angeles, Chicago, New York, and Toronto. The detection of VOCs and OVOCs utilized an H_3O^+, NH_4^+, and I^- chemical ionization mass spectrometer.

ERs are computed in relation to the enhancement of various other compounds, such as carbon monoxide, methane, and nitrogen oxides. Emphasis is placed on the consistency of ERs across different cities, and the impact of downwind chemistry on the observed trends. These findings represent the most comprehensive quantification of urban ERs to date, covering compounds that span a broad range of volatility for cities of different population density.

Figure 1: Overview of flights performed during the AEROMMA campaign [1] over cities of varying population density.

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Urban VOC Flux Observations Using PTR-TOF-MS

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Abstract

We have quantified the urban NMVOC flux using eddy covariance measurements as part of multiple field studies in Innsbruck since 2015. The seasonal and annual variation allows to investigate different urban emission sources (e.g. biogenic vs anthropogenic) and constrain the emission strength of different classes of VOC. Using a PTR-TOF-MS 6000 we can typically detect over 1300 ion masses exhibiting an upward (ie. net emission) flux. While individual NMVOC fluxes can be small, the sum can add up to a sizeable overall reactive carbon flux entering the urban atmosphere. For comparison, the total measured NMVOC flux using the PTR technique is comparable to the urban NO_x and CH_4 flux. In addition, we find compelling evidence that oxygenated non methane volatile organic compound emissions (OVOC) released into the urban atmosphere are significant, and that predictions of associated emissions are highly uncertain. These eddy covariance observations also allow to constrain VCP (volatile chemical product) emission fluxes in an urban setting, and quantitatively partition biogenic vs anthropogenic VOC fluxes. In view of globally accelerating urbanization, we argue that these types of observations are needed to re-evaluate the influence of urban NMVOC emissions on atmospheric chemistry, human health and the climate system.

Introduction

Based on current understanding, biogenic volatile organic compounds (BVOC) dominate the global budget of non-methane volatile organic compounds (NMVOC) released to the atmosphere. NMVOC play a crucial role for chemical processes in the lower atmosphere, influencing the oxidation (ie. self-cleaning) capacity of the atmosphere and contributing to secondary organic aerosol (SOA). Both processes are of important direct (e.g. through the formation of scattering and absorbing aerosol) and indirect (e.g. through the influence on the HO_x radical pool and the formation of ozone) consequence for maintaining the chemical stability of the atmosphere and thus influencing Earth’s climate. Recent evidence of a shift in anthropogenic VOC emissions [1,2]. towards different classes of primary VOCs released into the atmosphere, has sparked new interest in studying urban NMVOC emissions. As automotive emissions are thought to have come down significantly since the introduction of the three-way catalyst, the question of the significance of other consumer related product emissions (VCP) has raised new questions.

To that end fast online techniques such as PTR-TOF-MS can help to elucidate the emission strength of different NMVOC classes when combined with the eddy covariance (EC) method. Briefly, after Reynolds decomposition, the EC method allows determining the vertical flux of a component (F_c)

by measuring the covariance between vertical wind fluctuation (w’) and concentration fluctuation (c’):

$$F_c = \overline{w' \cdot c'} \qquad \text{(eq 1)}$$

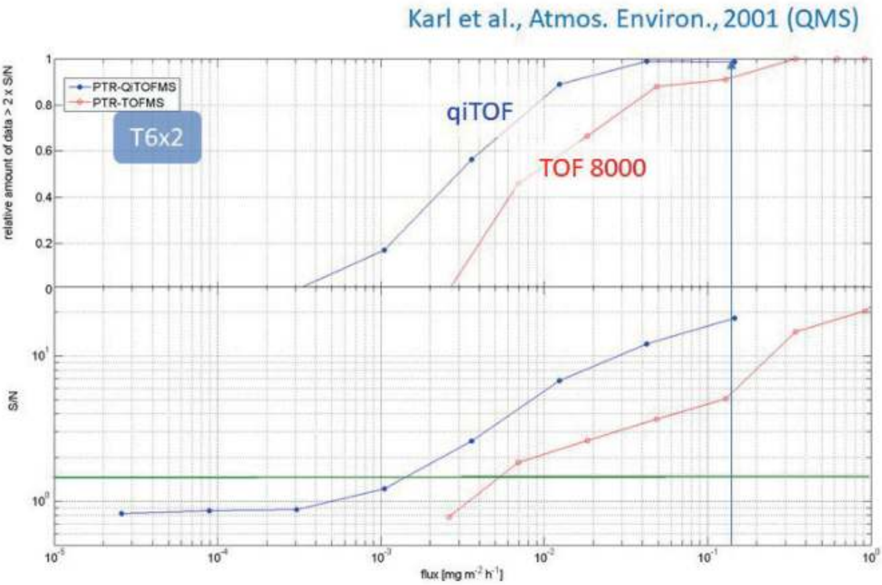

Figure 1: Fraction of flux data left above 2 x S/N ratio. Comparison between the first version of PTR-TOF-MS (TOF8000) (Müller et al., 2010) and the second generation with a quadrupole interface. Flux LOD’s for the newest generation (TOF T6x2) is indicated by the light blue box.

Important for these types of observations is to achieve high sensitivity over low internal instrument background. Since the first EC observations [3] (Fig.1) LOD for flux measurements have significantly improved from 0.1 mg/m^2/h to 1 x 10^{-5} mg/m^2/h for compounds like isoprene, benzene or toluene [4]. The sensitivity and LOD for PTR-TOF-MS applications have significantly improved over the past years, making it tractable for fast and accurate EC observations. Along with the technical improvement of TOF new demand for analysis codes for VOC EC analysis has also emerged [4]. Since the first EC observations using a PTR-QMS [3] (Karl et al., 2000 and 2001), TOF-MS technology has significantly enhanced the ability to detect a large number of compounds with the EC method. Over the past 2 decades direct flux observations using PTR-MS were performed above many different ecosystems and urban areas including ground and airborne platforms [1, 4-9] (e.g. Müller et al., 2010, Fischer et al., 2021; Langford et al., 2009; Park et al., 2013; Millet et al., 2018, Misztal et al., 2014, Karl et al., 2018). Here we give an overview over recent urban measurement campaigns in Innsbruck spanning several years.

Experimental Methods

Eddy covariance observations were performed on a 42 m high urban flux tower down town of Innsbruck, Austria (47∘15′51.66″ N, 11∘23′06.82″ E). The PTR instruments were housed on the uppermost level of the building close to the flux tower. On top of the tower a CPEC200 eddy covariance system was mounted which is a closed-path eddy covariance flux system allowing to measure turbulent quantities, CO_2 and H_2O. The VOC sample inlet line was colocated within ~15 cm distance of the sonic anemometer. VOC concentrations were measured using a PTR-QiTOF-MS and a PTR-TOF 6000 X2. The instruments were operated in hydronium mode at standard conditions in the drift tube allowing an E/N of about 112 Townsend. They were set up to sample ambient air from a turbulently purged and heated 0.375 in. Teflon line of 13.2 m length with a sampling flow of 18.9 slpm. Every 7 h, zero calibrations were performed for ~30 min, providing VOC-free air from a continuously purged catalytical converter though a setup of software-controlled solenoid valves. In addition, the instruments were calibrated with a suite of VOCs from a 1 ppm calibration gas standard (Apel & Riemer, USA) which was added to the VOC-free air and dynamically diluted into low ppbv mixing ratios. The data analysis with the InnFLUX code is described in detail by Striednig et al., 2020.

Results and Discussion

During a spring campaign in 2021 we found more than 1300 unique ions that are emitted into the urban atmosphere. Fig. 2 only depicts compounds for which we observe a net flux into the atmosphere. The Kendrick mass defect plot shows a significant amount of oxygenated species. High fluxes were also observed for aromatic compounds (BTEX), that fall along the horizontal line depicted in Fig. 2.

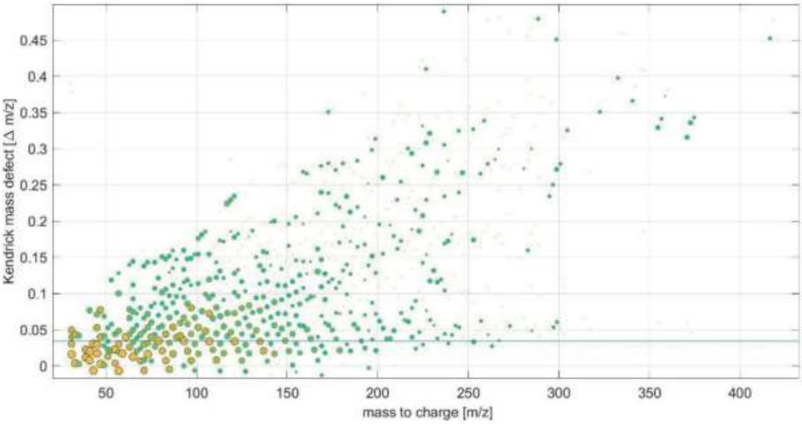

Figure 2: Kendrick mass defect plot depicting ions that exhibit a positive net flux out of the city. The size of the symbols scales with the flux. As an example, the blue horizontal line corresponds to the homologous series of aromatic compounds.

Benzene (and toluene) fluxes in Innsbruck are typically on the order of 0.05 – 0.2 nmol/m^2/s (0.1-0.4 nmol/m^2/s). In spring – time we observed lower emission fluxes of isoprene (and monoterpenes) 0.03 – 0.1 nmol/m^2/s (0.04 – 0.13 nmol/m^2/s) than in a summer campaign 2018. Spring time observations also show some anthropogenic contribution to compounds typically associated with biogenic emissions. While individual emission fluxes might appear small their sum adds up to a sizable observed NMVOC flux. In spring 2021 for example we obtain a median NMVOC flux of ~12 nmol /m^2/s, this is comparable in magnitude to the NO_x flux (~8 nmol /m^2/s) and the CH_4 flux (~10 nmol/m^2/s). Because the calculated covariance from EC corresponds directly to changes in emissions, variations on diurnal, weekly and seasonal time periods allow to construct models that allow deciphering anthropogenic and biogenic emission sources. The rich datasets generated by PTR-TOF-MS should also allow to provide chemical emission fingerprints that can be used to identify emission sources of other important gases, for example methane.

Acknowledgements

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Probing composition and sources of VOCs in 10 new apartments in Beijing, China

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Abstract

Volatile organic compounds (VOCs) emitted from building and furnishing materials represent a major concern of indoor air quality, in particular in new buildings. We carried out multi-week non-targeted VOC measurements in 10 new apartments in Beijing, China, using a Proton-Transfer-Reaction Quadruple interface Time-of-Flight mass spectrometer (PTR-QiToF). Non-targeted analysis suggests that chemical compositions of VOCs in these apartments were comparable to some extent, despite the differences in the furnishing materials and occupants' activity patterns. Indoor VOCs mainly came from indoor continuous emission. Moreover, a class of potential emerging pollutants, dibasic esters (DBE), were identified.

Introduction

On average, people spend ~90% of their time indoors. Volatile organic compounds (VOCs) represent a class of important air pollutants in the indoor environments. A main source of indoor VOCs is building and furnishing materials. Driven by development of new chemicals and materials as well as by environmental regulation, building and furnishing materials change over time. These changes in turn alter VOC composition in residences, offices, and schools, and thereby affect human chemical exposure.

China has been experiencing house booming since 1990s. A large variety of new building and furnishing materials emerge to meet different needs. VOC exposure in newly renovated urban residences has raised substantial public concern. Most previous VOC studies in new dwellings in China targeted for a few classic pollutants, such as formaldehyde, benzene, and toluene. Indoor VOC samples were often collected under closed-house condition and analysed offline in the laboratory, following the procedures in the National Indoor Air Quality Standard. There is a need to understand VOC composition under normal occupancy in new dwellings.

Herein we report real-time VOC measurements in 10 new apartments in Beijing, China, using a Proton-Transfer-Reaction Quadruple interface Time-of-Flight mass spectrometer (PTR-QiToF). Non-targeted analysis was conducted to examine overall feature of VOC composition across apartments. Some potential emerging pollutants were identified.

Experimental Methods

We carried out two indoor air observational campaigns in a new residential complex in Beijing in 2019-2020, each targeting on five apartments in a differing building. The residential complex was built at the end of 2018. The home owners finished and furnished their individual apartments in early 2019. Our first campaign (fall) was from mid-September to early November 2019, and the second (winter) was from mid-December 2019 to mid-January 2020. All the apartments were fully finished and furnished by the time of respective campaign, and many were already occupied.

PTR-Qi-ToF and some other gas analyzers (e.g., O_3, NH_3/NO_x) were situated in a vacant apartment and sampled air in the other four apartments and outdoors through heated and insulated sampling inlets (1/4" OD PFA). Eight inlets were installed in fall campaign and six in winter, including one or two inlets in each apartment (in the living room or in a bedroom) and one outdoors. Air was continually pulled through the sampling inlets. Online instruments were sequentially subsampled from each of six selected inlets for a 5-minute period using a six-way solenoid valve (interior surface of PTFE) with a measurement cycle of 30 minutes. To reduce the memory effects of VOCs related to sample switching, the last 3 of every 5 mins were averaged and taken for data analysis.

Results and Discussion

There were 218-229 VOC signals detected in the five apartments investigated in the fall, with 147 signals in common. The number of VOC signals detected increased to 247-255 in the apartments investigated in the winter, with 216 in common. Top five VOC signals detected in individual apartments overlapped. Methanol, acetaldehyde, and acetone are among the top five lists in all apartments. For most VOC signals, time-averaged concentration varied within a factor of four across different apartments investigated in each season. These results suggest that chemical composition of VOCs in the investigated apartments were comparable to some extent, despite the differences in the furnishing materials and occupant activity patterns. Further analysis on indoor-to-outdoor ratios and temporal pattern of indoor VOCs suggests that indoor VOCs mainly came from indoor continuous emission. Only a small number of VOCs were mainly contributed by outdoor sources and intermittent indoor emission. Moreover, the signal ratios of some VOCs were consistent across different apartments, which suggests that they may have similar sources.

A group of seldomly reported VOC signals ($C_xH_{2x-1}O_4^+$ and $C_{x-1}H_{2x-5}O_3^+$, x=6-8) were observed in 3 out of 10 apartments [1]. They were attributed to dimethyl esters of succinic, glutaric, and adipic acids, which are rarely known for their presence in indoor air. This attribution was confirmed using authentic standards and by supplementary gas chromatography/mass spectrometry analysis. Despite varying concentrations, the three compounds exhibited largely consistent ratios across the three apartments and throughout the observation periods. The observed ratios resemble chemical composition of dibasic esters (DBE), which are solvent mixtures made of the three compounds and have been increasingly used in coating industry. Field "sniffing" experiment further confirms DBE emission from the coating of some wooden furniture in at least one apartment. The average airborne DBE concentrations in the three apartments were 41, 5, and 4 μg/m^3, respectively, exceeding the screening level of 1 μg/m^3 recommended by the Michigan Department of Environmental Quality, US. In the context of fast-growing DBE usage, the current results suggest that DBE might be emerging indoor air pollutants and merit further investigation.

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Closing the forest-atmosphere flux budget for VOCs and ozone

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Abstract

Forest-atmosphere exchange plays a major role in modifying the chemical properties of the atmosphere. In particular, the terrestrial biosphere is simultaneously a major source and a major sink of volatile organic compounds (VOCs) to and from the atmosphere. With up to 10^5 different organic species thought to exist in the atmosphere, there are major open questions regarding the number of VOCs undergoing surface-atmosphere exchange and the main environmental factors driving that exchange. These uncertainties limit our understanding of the overall VOC budget and of their broader impacts on ozone (O_3), aerosols, and atmospheric oxidation.

At the same time, forest-atmosphere exchange affects the O_3 budget directly via dry deposition, which is the second-largest O_3 sink in the troposphere. Predictions of O_3 deposition and near-surface concentrations have been limited by the crude deposition schemes commonly employed in chemical transport models and by the uncertain importance of non-stomatal uptake and in-canopy VOC + O_3 chemistry for the overall flux.

Here, we present the most comprehensive ecosystem-scale VOC flux measurements to date, obtained by applying the eddy covariance technique to spectra collected simultaneously using dual high-resolution time-of-flight mass spectrometers. We use the results to test current understanding of VOC flux drivers and the importance of previously unknown or unmodeled compounds. We further combine these results with simultaneous, vertically resolved, flux and gradient measurements for O_3 to 1) evaluate current model predictions of ozone uptake, and 2) quantify the importance of different uptake pathways and in-canopy VOC chemistry for near-surface ozone removal.

Ultrahigh Sensitivity PTR-MS Instrument with a Well-Defined Ion Chemistry

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Abstract

Condensed polycyclic aromatic hydrocarbons (PAHs) are a group of highly toxic organic compounds that are formed naturally through incomplete combustion of organic materials and are also released through anthropogenic sources such as industrial processes, transportation, and waste incineration. Exposure to high levels of these compounds is harmful to human health, because of its mutagenic, carcinogenic, teratogenic, and immunotoxicogenic effects. But even at exposure levels as low as 1 ng m^{-3} of the commonly found PAH benzo(a)pyrene, they can be detrimental to human health. However, detecting these compounds can be challenging due to the semi-volatile nature and low proton affinity of the most abundant PAHs. Typical detectors for PAHs are HPLC or GC, but these methods have low time resolution and are prone to sampling artefacts [1]. Other real-time methods like CIMS cannot or only hardly detect and quantify PAHs.

Proton transfer reaction mass spectrometry (PTR-MS) has already proven to be able to detect condensed PAHs at low concentrations on a molecular composition level [2]. PTR-MS is a soft chemical ionization technique that can quantitatively detect a plethora of volatile organic compounds (VOCs). With the renowned CHARON particle inlet for PTR-MS, this capability is expanded to the particle phase. The setup consists of a denuder to remove the gas phase, an aerodynamic lens system for particle enrichment and a thermal desorption unit for vaporization of the molecular constituents of the non-refractory particles.

Hence, side-by-side measurements of CHARON PTR-TOF and filter samples at the TROPOS operated research station Melpitz, Germany, resulted in good agreement on a 24h basis, while CHARON PTR-TOF was able to provide significantly more temporal information [3].

Herein we present a new generation PTR-TOF instrument that combines a clean Fast-SRI ion source, a radio-frequency ion molecule reactor (“FUSION”) and a high resolution TOF-MS (mass resolution >10k). This FUSION PTR-TOF 10k instrument reaches unprecedented sensitivities up to 80 000 cps $ppbV^{-1}$ and limits of detection (LOD) < 1 pptV in 1 s [4]. The original setup was successfully modified to reduce sample flow and now allows for coupling of a CHARON particle inlet including an aerodynamic lens system. Consequently, LODs are further improved by a factor 20 for particles in the size range of 100-1000 nm. This high time resolution CHARON FUSION PTR-TOF 10k allows for the real-time detection of condensed PAHs on a molecular composition level, well below harmful exposure levels with 1-min LODs down to low pg m^{-3} levels.

To demonstrate the outstanding capabilities of this new instrument, we present a first characterization of ambient organic aerosol in Innsbruck, Austria. From this dataset, a series of PAHs is identified and time-series of lowest mass concentrations are determined. We found 1-min LODs for $C_{16}H_{10}$ (i.e. pyrene, fluoranthene) and $C_{20}H_{12}$ (e.g., benzo-pyrene, benzo-fluoranthene) of 70 and 25 pg m^{-3}, respectively. Exemplary mass spectra of two selected PAH signals with their corresponding time-series as measured in Innsbruck, Austria, in August 2023 are shown in Figure 1. Subsequently, matrix factorization is applied, delivering insight into separate sources of PAHs.

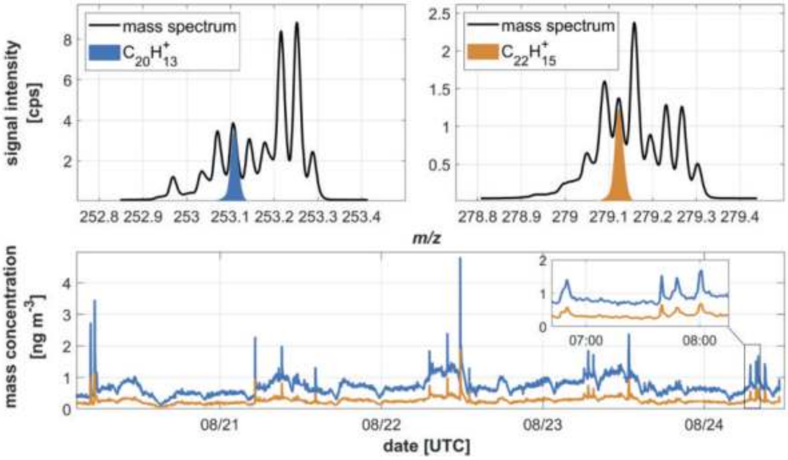

Figure 1: Two selected PAH signals with the corresponding time series as measured in Innsbruck, Austria, in August 2023.

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Airborne flux measurements for validation of VOC emission inventories and source attribution

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Abstract

For accurate prediction and modelling of air quality and climate, it is necessary to understand the emissions of volatile organic compounds (VOCs) from the potpourri of sources that they are emitted from: traffic, industry, households, plants, agriculture, etc. In the past, efforts to understand the magnitude and composition of VOC emissions have often relied on indirect methods – either using bottom-up emission models, or inferring emissions top-down from concentration measurements via chemical transport models. Both approaches rely on a number of assumptions regarding chemical reactions and transport - and thus are subject to large uncertainties.

Airborne flux observations provide direct emission and deposition information at landscape scale with a resolution of a few km. We performed airborne eddy covariance measurements of a large range of VOCs on board a Twin Otter aircraft in Los Angeles [1] and the agricultural San Joaquin Valley [2] in California using PTR-ToF-MS. Combining these observations with a footprint model, we matched them with gridded inventories in space and time. The comparison with the inventories showed a good representation of typical traffic VOCs but a significant underestimation of oxygenated VOCs (likely from volatile chemical products and cooking) and terpenoids by the inventories.

Using airborne flux footprints in combination with landcover information of the San Joaquin Valley, we disaggregated the observed VOC emissions by multivariate linear regression and attributed them to their sources. This way, we obtained typical VOC emission rates and composition for dairy farms, citrus crops, citrus processing facilities, oak forests, oil and gas wells, and urban areas.

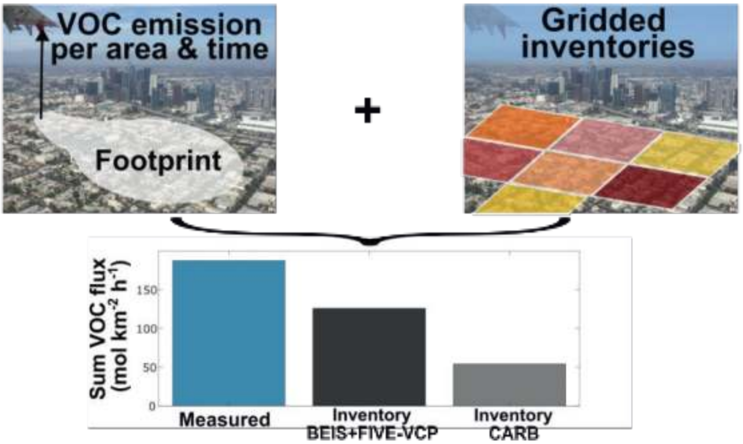

Figure 1: Schematic of the approach comparing airborne VOC flux measurements with gridded emission inventories as done for Los Angeles in [1]. Figure under creative commons license (CC-BY 4.0) from [1].

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Volatile organic compound fluxes from Amazon rainforest soil

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Abstract

Volatile organic compounds (VOCs) play a crucial role in chemical reactions within the atmosphere, influencing air quality, cloud formation, and climate. Soils can both emit and consume VOCs, contributing significantly to ecosystem-scale VOC emissions.

In this study, we continuously monitored VOC fluxes from the soil of the Amazon rainforest by means of a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) directly connected to an automated soil flux measuring system.

The Amazon rainforest soil was a net sink for isoprene and, simultaneously, a net source for monoterpenes and sulfur-containing compounds, namely methanethiol and dimethyl sulfide. Soil microbial activity, soil physicochemical properties, VOC ambient concentrations, and soil litter content were the main drivers of the observed soil VOC fluxes.

The results show that the Amazon rainforest soil represents an important component of the overall ecosystem VOC dynamics. Soil VOC fluxes and their parameterization related to environmental parameters must be included in atmospheric models to simulate current atmospheric chemistry and to improve climate model predictions of ecosystem response to climate change.

Introduction

The tropical rainforests are the world's largest source of biogenic volatile organic compounds (VOCs) to the atmosphere [1]. VOCs play an important role in atmospheric processes, as their oxidation products drive the production of secondary organic aerosol (SOA) particles. These particles, in turn, can influence cloud formation, the earth's radiative balance and, consequently, the climate [2]. Soils can act both as a source and a sink of atmospheric VOCs, and their contribution to the atmospheric VOC budget may be comparable to that of plants [3, 4]. Soil VOC fluxes are challenging to constrain because they result from a combination of numerous biotic (e.g., soil microbial activity) and abiotic (e.g., soil temperature, soil moisture) factors [5-7]. Therefore, the composition, magnitude, and direction (i.e., emission vs uptake) of soil VOC fluxes depend on ecosystem type, season, diel dynamics, and environmental conditions [8, 9]. In this study, VOC fluxes from the soil of the Amazon rainforest were continuously measured by means of a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) connected to an automated soil flux measuring system. Additionally, soil respiration (soil CO_2 emission flux), soil temperature, soil moisture, and soil physicochemical properties were measured, and their effects on soil VOC flux dynamics were thoroughly analyzed.

Experimental Methods

For soil VOC fluxes measurement, the inlet of the PTR-ToF-MS (PTR-ToF 4000, Ionicon Analytik GmbH, Innsbruck, Austria) was connected to the outflow of an automated closed dynamic soil flux measuring system consisting of a LI-870 infrared gas analyzer (IRGA; for CO_2 fluxes measurement), a LI-8250 8-port multiplexer (Licor Inc., Lincoln, NA, USA) and 4 dynamic soil flux chambers (LI 8200-104 Long-Term Chambers with opaque lids, Licor Inc.). To prevent negative pressure in the soil flux measuring system, the air sampled by the PTR-ToF-MS was replaced by introducing an equivalent amount of synthetic air into the system. In order to minimize surface effects on VOC analysis, perfluoroalkoxy (PFA) tubing was used for the soil flux measuring system and for the PTR inlet.

Three long-term chambers were placed on PVC collars installed on three different types of soil: bare organic soil, bare clay soil, clay soil with litter. One chamber was placed on PFA foil and used as blank. Soil chambers were measured consecutively and each chamber measurement consisted of 3 minutes of pre-purge during which the chamber lid was open and lines were flushed with the ambient air; 6.5 minutes of soil flux measurement during which the chamber lid was closed; 3 minutes of post-purge during which the chamber lid was open and lines were flushed with the ambient air. Soil VOC fluxes were calculated from the slope obtained by applying the linear regression of the VOC concentration versus the time during the 6.5 minutes of chamber closure. All fluxes were corrected for dilution resulting from the PTR-ToF sampling volume replacement with synthetic air [7].

Results and discussion

Soil gas flux rates were markedly different between the three extremes of soil, highlighting the impact of soil physicochemical properties on soil gas fluxes.

Soil respiration (CO_2 soil emission flux) measured from the bare organic soil and clay soil with litter was approximately 35 and 10 times higher, respectively, than that from the bare clay soil. This reflects higher soil microbial activity in soils with a greater organic substrate available [10]. The soil of the Amazon rainforest acted as a net sink of isoprene (Figure 1). Similar to the soil respiration, the highest isoprene uptake rates were observed in the bare organic soil, while the lowest rates occurred in the bare clay soil. This correlation indicates a link between the soil uptake of isoprene and soil microbial activity [7]. Soil uptake rates of isoprene showed a diel cycle that was driven by isoprene atmospheric concentration. This is because plant emissions of isoprene are metabolically linked to plant photosynthesis with higher emission at higher photosynthetic rates [7]. As a result, atmospheric concentrations of isoprene are higher during daytime than at nighttime.

Monoterpenes were emitted by rainforest soil, with the highest emissions observed from the clay soil with litter, indicating that they were mainly generated from litter degradation. Monoterpenes emissions increased with the temperature, reflecting higher litter degradation as soil temperature increased.

The Amazon rainforest soil was also a source of sulfur containing compounds, namely methanethiol and dimethyl sulfide. The highest soil emissions of sulfur compounds were observed from the clay soil with litter, suggesting that they were generated from litter degradation. Significant soil emissions of dimethyl sulfide were also observed from the bare clay soil following a rain event. In this type of soil, the rain water could have induced mobilization and mineralization of the soil organic sulfur pools, leading to the production of dimethyl sulfide [7].

The results show that the Amazon rainforest soil is essential to the overall ecosystem VOC budget. Future experiments will be focused on long-term soil VOC flux measurements to investigate their dependence on enviromental variables. Soil VOC fluxes will be then included in atmospheric models to simulate current atmospheric chemistry and to improve climate model predictions of ecosystem response to climate changes.

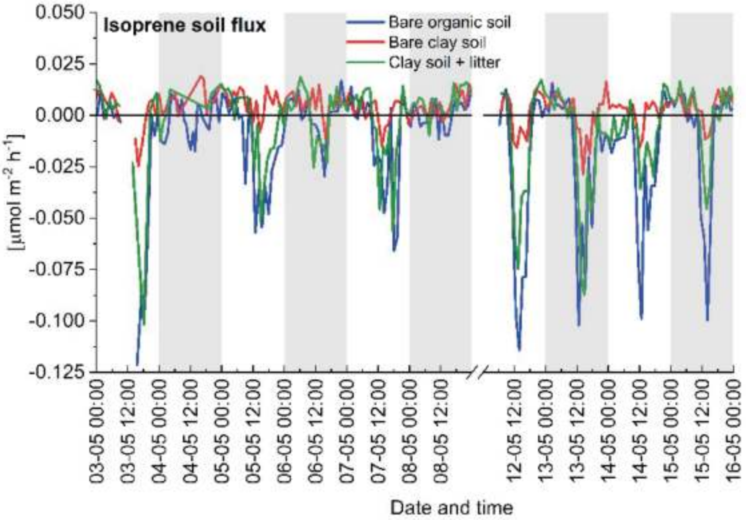

Figure 1: Isoprene fluxes measured from the Amazon rainforest soil over the period 3 – 16 May 2022. Bare organic soil (blue), bare clay soil (red), clay soil with litter (green).

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Soil – an important sink for VOCs?

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Abstract

The role of soils as sources and sinks for volatile organic compound (VOC) is poorly understood. Here, we assessed the VOC exchange processes in two different upland soil types, one from a temperate beech forest and another from a heather heath. We incubated the soil samples under different conditions in the laboratory using a dynamic flow-through system and proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS). We show that the two contrasting soil types naturally emit different VOC blends, and that the emissions are influenced by soil properties, temperature, and oxygen availability in the soil. When VOCs were introduced to the incubation headspace, the soils acted as sinks for most VOCs. The uptake rate of VOCs increased with the available VOC concentration in the headspace and with temperature. Overall, our study highlights the bidirectional nature of soil VOC exchange as part of the biogeochemical cycling of VOCs in ecosystems.

Introduction

Natural ecosystems emit approximately 1000 Tg of carbon as VOCs annually, influencing tropospheric air quality and Earth's radiative balance. While plant VOC emissions are extensively studied, soils have received less attention. Soil-atmosphere VOC exchange is complex, and influenced by various processes and factors, such as plant roots, microbial activity, and abiotic processes [1].

VOC uptake by soil involves physical, chemical, and biological factors that influence the direction and strength of the net VOC fluxes. VOC uptake has been shown to be a microbial process [2], but dissolution in soil water and adsorption to soil particles could also contribute to the uptake. The uptake is thus likely affected by soil physical properties, organic matter composition, temperature, water/oxygen content, and microbial community composition and biomass. To provide process understanding on soil VOC dynamics, we conducted a study under controlled conditions to assess net VOC production and uptake rates in response to different VOC concentrations, oxygen availability, and temperature.

Experimental Methods

Soil samples

Soil samples were collected from a beech (*Fagus sylvatica*) forest and heather (*Calluna vulgaris*) dominated heath ecosystem in Denmark. The soil samples were sieved, homogenized, and analyzed for chemical and biological properties by standard methods (see [3] for details).

Incubation experiments

Soil samples were incubated in glass jars under controlled conditions in a dynamic flow-through system. Desired concentrations of VOC mixtures in water consisting of 12 compounds (methanol, acetaldehyde, acetone, isoprene, 2-butanone, 2-methylfuran, toluene, furfural, cis-3-hexen-1-ol, benzyl alcohol, terpinolene, and linalool) were vaporized and supplied to the incubation jar headspace with a liquid calibration unit (LCU-a, Ionicon Analytik, Innsbruck, Austria). The headspace outflow VOC concentrations were monitored using a PTR-ToF-MS instrument (TOF-1000 *ultra*, Ionicon Analytik, Innsbruck, Austria).

Experiments were conducted at different VOC supply concentrations (all at pptv levels). Further, experiments were conducted at three different temperatures (7 °C, 13 °C, and 19 °C), and using either synthetic air or pure nitrogen as the inflow gas into which VOCs were supplied. Finally, we conducted a control experiment using sterilized glass beads instead of soil in the incubation jars to estimate physical adsorption of VOCs to inorganic soil matrix.

Results and Discussion

When VOC-free air or nitrogen gas was introduced to the soil incubations, the soils emitted a diverse mixture of VOCs, with acetone as the most emitted compound [3]. The emission rates were overall higher in the heath soil than in the forest soil, which was more nutrient rich and had higher microbial biomass.

When VOCs were supplied to the headspace, the net VOC emission turned into net VOC uptake, the rate of increased with supplied VOC concentration [3]. The VOC uptake also increased with temperature, but our results from the comparison of aerobic and anaerobic conditions were less conclusive. The physical adsorption of VOCs to glass beads was minimal compared to the soil uptake, which was likely driven by microbial metabolism of VOCs. Microbial uptake of VOCs likely regulates net emissions from decomposing leaf litter or thawing permafrost, but we know little about the sink capacity of soils in uptake of plant-produced VOCs. Our study showcases the potential importance of VOC uptake processes that need to be better understood to allow modeling of VOC exchange in ecosystems.

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Bacteria isolated from Arctic soil crust and permafrost produce volatile sulfur and nitrogen compounds in vitro

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Abstract

We have measured *in vitro* the volatile fingerprints of two bacterial species isolated from permafrost and soil crust in Northern Greenland. Proton-transfer-reaction mass spectrometry (PTR-MS) was used to monitor the real-time emissions of volatile organic compounds (VOCs) by the studied bacteria throughout the culturing. Gas chromatography mass spectrometry (GC-MS) was subsequently used to concretely identify compounds of interest. Principal component analysis (PCA) was used to estimate the differences between the volatile fingerprints of the studied bacteria, while dynamic production profiles were used to link the VOC production to the bacterial life cycle.

We found clear differences between the volatiles produced by *Arthrobacter* sp. and *Oceanobacillus* sp. Some of the most abundantly produced compounds by *Oceanobacillus* sp. were methanethiol and dimethyl sulfide (DMS), known contributors to the formation of sulfuric acid in the atmosphere. The production capacity of methanethiol by *Oceanobacillus* sp. *in vitro* was significant. *Arthrobacter* sp. produced a wider variety of compounds, but less abundantly. Organic nitrogen compounds, such as pyrrole and pyrazines, were characteristic of *Arthrobacter* sp. *in vitro*. The dynamic production profiles, combined with bacterial growth-curve measurements, revealed that certain compounds are clearly linked to the active growth of the bacteria, while others are only produced in the stationary or death phase.

Our results show that the studied Arctic bacteria produce a variety of VOCs, some of them in large concentrations, when suitable organic material is present. Clear differences in the volatile fingerprints of *Arthrobacter* sp. and *Oceanobacillus* sp. indicate differing metabolic activities, possibly due to adaptation to their environments – permafrost and soil crust, respectively. These findings shed light on the emission pathways and capacities of bacterial species living in the Arctic regions, which are still poorly understood. Furthermore, as some compounds in this study are clearly connected to active bacterial growth, they could be used in the future as indicators of changes in the composition and activity of bacterial communities in the Arctic soils and permafrost.

Introduction

Permafrost, ground which has remained frozen for two or more years, covers 12-18% of the exposed land surface area of the Northern Hemisphere [1]. Large amounts of undecomposed organic material is trapped inside permafrost, where bacterial activity remains low due to the low temperatures. Because of climate change, however, the Arctic warms at least two times faster than the global average which causes the accelerated thawing of the permafrost, and consequently, more favorable environment for bacteria [2,3]. As the Arctic keeps warming, the increased bacterial activity starts decomposing the available organic material inside permafrost, and ultimately, releases yet to be known amounts of greenhouse gases and VOCs into the atmosphere [4,5,6]. Understanding the emission and consumption pathways and capacities of bacteria living in the Arctic soil and permafrost is vital for predicting both "what" and "how much" will be released in the future [7]. However, at the moment these factors are poorly known. To shed light on this matter, we have studied the VOCs produced *in vitro* by two bacterial species isolated from permafrost and soil crust in Northern Greenland.

Experimental Methods

The studied bacteria *Oceanobacillus* sp. and *Arthrobacter* sp. were cultured in minimal medium with different salt (NaCl) concentrations. Pure nutrient broth was used as a control. Growth curves (optical density at 600 nm, OD_{600}) were measured for parallel cultures simultaneously with the cultures undergoing VOC measurements.

Volatiles produced by the bacteria *in vitro* were measured continuously throughout the culturing with PTR-MS (PTR-TOF 1000 ultra, IONICON). An automated valve system was used to rotate between the different samples for a total of 60 h. Identities of compounds of interest were also further confirmed with GC-MS. Principal component analysis (PCA) was used to analyze the separation between the two bacterial species according to the VOCs produced.

Results and Discussion

We found clear differences between the volatile fingerprints of *Oceanobacillus* sp. and *Arthrobacter* sp. In general, *Oceanobacillus* sp. produced a variety of organic sulfur compounds and chloromethane, while *Arthrobacter* sp. produced organic nitrogen compounds, ketones, and aldehydes. Some of the main separators between species were methanethiol, DMS, dimethyl disulfide (DMDS), dimethyl trisulfide, and chloromethane produced by *Oceanobacillus* sp., and pyrrole, dimethylamine, trimethylpyrazine, 2,5-dimethylpyrazine, pyrazine, methyl vinyl ketone, 2-methylpropanal, butanal, hexanone, and hexanal by *Arthrobacter* sp. Additionally, continuous monitoring of the produced volatiles in combination with bacterial growth curve measurements from parallel cultures, showed different compounds are produced in different parts of the bacterial life-cycle. For example, methanethiol is clearly linked to the active growth of *Oceanobacillus* sp., while the production of DMDS starts significantly later in the stationary phase. Our results indicate significant differences in the metabolic functions of the studied bacteria – perhaps due to living in different Arctic environments. Furthermore, we show that environmentally important VOCs, such as DMS and methanethiol, are produced abundantly *in vitro*.

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Fate of dimethyl sulfide at cold temperatures

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Abstract

Dimethyl sulfide (DMS), emitted from the ocean, contributes via its oxidation products significantly to sulfate aerosol formation. We investigated OH-initiated DMS oxidation with different highly-sensitive chemical-ionization methods in free tropospheric air masses reaching a mountain top station in Bolivia at 5200m a.s.l. from the Pacific and in the laboratory at the CERN-CLOUD chamber over a large temperature range. We further observed low sulfuric acid (H_2SO_4) to methane sulfonic acid (MSA) ratios at low temperatures in the CLOUD chamber that are in line with remote coastal atmospheric observations and suggest an MSA formation pathway via the addition channel. The CLOUD results shine light onto the high concentrations of dimethyl sulfone ($DMSO_2$) observed in the free troposphere.

Introduction

Dimethyl sulfide (CH_3SCH_3, DMS,) is the main natural contributor to atmospheric sulfur[1, 2] with its estimated global flux ranging between 18 and 34 Tg S year^{-1} [2]. Its oxidation products sulfuric acid (H_2SO_4) and methane sulfonic acid ($CH_3S(O)(O)OH$, MSA) [1, 3] contribute to aerosol formation. More direct atmospheric observations of DMS and its oxidation products are needed to constrain the effects of DMS on climate [4].

Also the DMS oxidation scheme is still under investigation: The recently observed autoxidation channel leading to $HOOCH_2SCHO$ (HPMTF) [5, 6] has not yet been investigated as a function of temperature. Only recently, sulfuric acid and MSA formation via the radicals CH_3SO_2 and CH_3SO_2OO has been directly observed [7]. In cold and remote coastal regions of the atmosphere, the sulfuric acid to MSA ratio has been observed to be lower than simulated by previous DMS oxidation schemes. Therefore, controlled DMS oxidation experiments under a wide range of temperatures are needed to better constrain product and aerosol yields.

Experimental Methods

We investigated DMS oxidation under a variety of different conditions both, as observed in the real atmosphere and in the CLOUD chamber (temperature ranging from +25°C to -10°C) with the help of highly-sensitive chemical ionization mass spectrometers, using a wide range of primary ions such as nitrate, bromide, iodide, and others. The PTR3, using either $(H_2O)_nH_3O^+$ (n = 0,1,2,3) or $(H_2O)_n(NH_3)_mNH_4^+$ (n, m = 0,1,2) as primary ions.

The atmospheric measurements took place at the Chacaltaya GAW station near a mountain top in Bolivia at 5200 m a.s.l.. During dry season (May-November) , the station typically receives air masses from the west, influenced by the surrounding altiplano at daytime but often above an inversion layer during nighttime. To identify source regions, we performed a statistical analyses of Lagrangian backtrajectory calculations over a cylindrical domain of 1600 km diameter.

During both CLOUD chamber and atmospheric measurements, the PTR3 was calibrated with hexanone, acetonitrile, alpha-pinene and trimethyl benzene on a regular basis at least every few days. Other CIMS instruments were characterized before and after the measurement period, using quantitative sulfuric acid production. Further offline-calibrations of observed key species and tests of all instruments complimented the work during the campaign and instrument-comparisons helped in determining quantification uncertainties.

Results

At the Chacaltaya GAW station at 5200 m a.s.l., we observed especially $DMSO_2$ in the gas-phase at a few ppt, but also DMSO ($CH_3S(O)CH_3$), MSIA ($CH_3S(O)OH$), CH_3SCHO, CH_3SOH, MSA, and H_2SO_4 (see Fig. 1 [8]). These observations were only possible due to the low limits of detection of the available high-end instrumentation. We divided the airmasses into clean free tropospheric (FT) and boundary-layer-influenced (Bl_{night} and Bl_{day}). In contrast to most detected signals, that strongly increase with the influence of the boundary layer, the DMS oxidation products do not show a strong dependence on the influence of the boundary layer.

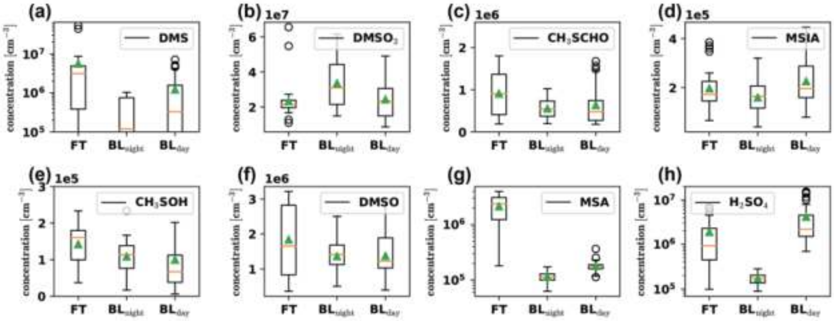

Figure 1: Observed gas-phase concentrations under standard conditions (e.g. 2.47e7 cm^{-} = 1 ppt) of DMS and its oxidation products measured by the PTR3 (DMS, DMSO, $DMSO_2$, MSIA, CH_3SCHO and CH_3SOH) and by the Nitrate-CIMS (MSA and H_2SO_4) [8]

Locally measured indicators such as a very low humidity, background black carbon concentrations and particle mass proved a negligible influence of local emission sources during the clean events. These indicators together with backtrajectory calculations showing an air mass descent down from 6-8 km a.s.l over the Pacific towards the station allowed the conclusion, that the air masses labelled as clean free tropospheric (FT) were not influenced by ground-level emissions for more than 4 days before they reached the measurement station.

In the particle phase, we observed methane sulfonate ($CH_3SO_3^-$, MS^-). Its concentrations on the filters correlate with the predominant wind direction coming from the Pacific. Unfortunately, both the gas-phase sulfuric acid concentration and the sulfate concentration in the particle phase were dominated by continuous volcanic sulfur degassing in heights above the stable inversion layer, which inhibited a discussion of the sulfuric acid to MSA ratio regarding the DMS chemistry.

In our laboratory study at the CLOUD chamber, we investigated the DMS chemistry under well-controlled conditions over a large temperature range (25°C to -10°C) and based an updated DMS oxidation mechanism on these data [9]. Figure 2 shows the H_2SO_4 to MSA ratio from coastal measurements together with our experiments at the CLOUD chamber, and calculated from 3 different DMS oxidation mechanisms. Our mechanism includes a potential MSA production from MSIA, which is formed after addition of OH to DMS, a pathway that is enhanced at cold temperatures.

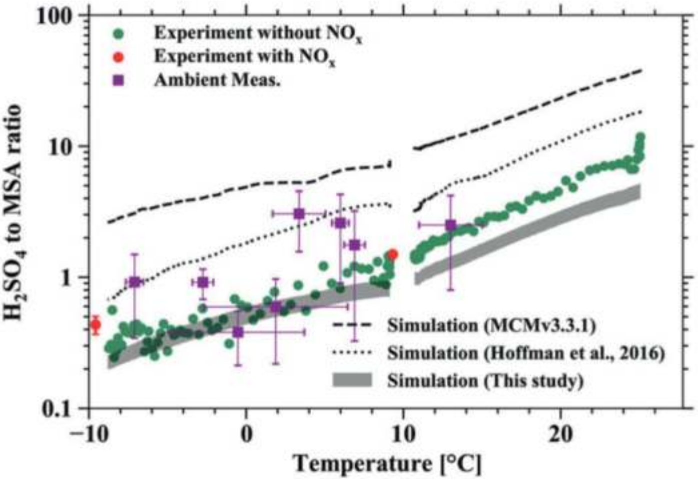

Figure 2: Observed ratio of gas-phase H_2SO_4 to MSA ratio in cold coastal environments (Arctic, Antarctic, Ireland) and in the CLOUD chamber, shown together with simulated ratios from two previous and our updated chemical mechanism [9]

Our model also takes into account the interface chemistry at the CLOUD chamber walls to allow a distinction into gas-phase and liquid-phase impacted products. Both MSA and H_2SO_4 were formed in the gas phase from DMS oxidation and had a loss term due to the uptake at the stainless steel walls. However, we observed a strong surface-assisted production of gas-phase $DMSO_2$.

Discussion

At Chacaltaya, sulfate and H_2SO_4 appeared impacted by volcanic emissions, but the other products can still give us an insight into DMS oxidation. Remarkable is the dominance of gas-phase $DMSO_2$ in both the free tropospheric measurements and the CLOUD chamber. Even when considering the MS^- concentrations in the particle-phase, $DMSO_2$ carries as much sulfur to the station in the gas-phase as is stored as MS^- in the particle-phase. In the CLOUD chamber, we showed, that the formation of $DMSO_2$ is driven by interface chemistry. A box model without interfaces lead to orders of magnitude smaller $DMSO_2$ concentrations compared to MSA. As the condensation sink is very small outside of clouds, it is likely that a large fraction of the $DMSO_2$ observed in the free troposphere might have been produced upon convective lifting of DMS, pushing a large fraction of the DMS-derived sulfur into this long-lived sulfur reservoir species.

At Chacaltaya, the observed concentrations of DMS oxidation products are too small in comparison to other condensible species observed during daytime to strongly impact the day-time particle formation or early growth. To quantify the impact of DMS oxidation on particle formation in those altitudes in clean air close to the marine outflow, further laboratory studies on particle formation with varying MSA and sulfuric acid concentrations as well as flight campaigns closer to marine outflow with modern low-detection-limit proton transfer and nitrate cluster reaction mass spectrometers are needed in combination with chemical aerosol characterization.

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Trace gas exchange by subarctic vegetation under global climate change

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Abstract

Biogenic emissions of volatile organic compounds (BVOCs) are a crucial component of biosphere-atmosphere interactions. In northern latitudes, climate change is amplified by feedback processes in which BVOCs have a recognized, yet poorly quantified role, mainly due to a lack of measurements and concomitant modelling gaps. Our recent studies have shown that high latitude vegetation possesses the potential to substantially boost its isoprene emissions in response to future rising temperatures, at rates that exceed the current Earth system model predictions [1-2].

Here, we present the first preliminary results of our latest field campaigns in a mountain birch forest in Northern Sweden. We used Proton Transfer Reaction–Time of Flight–Mass Spectrometry (PTR–TOF–MS) and eddy covariance to measure the ecosystem-scale fluxes of VOCs, together with the fluxes of CO_2 and H_2O, during the recent record-breaking heat episodes in the region. Our project also aims to observe and model the effect of herbivore insect defoliating outbreaks on the gas exchange of the forest.

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Quality assurance of volatile organic compounds within the atmospheric research infrastructure ACTRIS

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Abstract

The Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) is a pan-European research infrastructure (RI) producing high-quality data and information on short-lived atmospheric constituents. The data quality assurance is maintained by central facilities, i.e. in the case of reactive trace gases by the ACTRIS Centre for Reactive Trace Gases In Situ Measurements (CiGas). Proton Transfer Reaction Mass Spectrometry is an essential method for the detection of Volatile Organic Compounds (VOC) within ACTRIS. It is supported by CiGas through dedicated measurement guidelines, training activities, round robins and intercomparison campaigns to maintain high quality standards on the data products. The activities of CiGas are described in detail to promote common QA/QC routines for PTRMS-measurements and assure compatibility of the data being produced.

Introduction

Aerosol, Clouds and Trace Gases Research Infrastructure

The Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) [1] is the pan-European research infrastructure (RI) producing high-quality data and information on short-lived atmospheric constituents and on the processes leading to the variability of these constituents in natural and controlled atmospheres. ACTRIS produce high-quality assured datasets in the area of atmospheric sciences fulfilling the FAIR data principles (findability, accessibility, interoperability, reusability) and provide services, including access to instrumented platforms, tailored for scientific and technological usage.

Centre for Reactive Trace Gases In Situ Measurements

Within ACTRIS the data quality assurance is maintained by central facilities, i.e. in the case of reactive trace gases by the Centre for Reactive Trace Gases In Situ Measurements (CiGas) [2], a consortium of six European partner institutions, which combine complementary expertise on non-methane hydrocarbons, oxygenated VOCs, condensable vapors and nitrogen oxides (NOx) (Fig. 1).

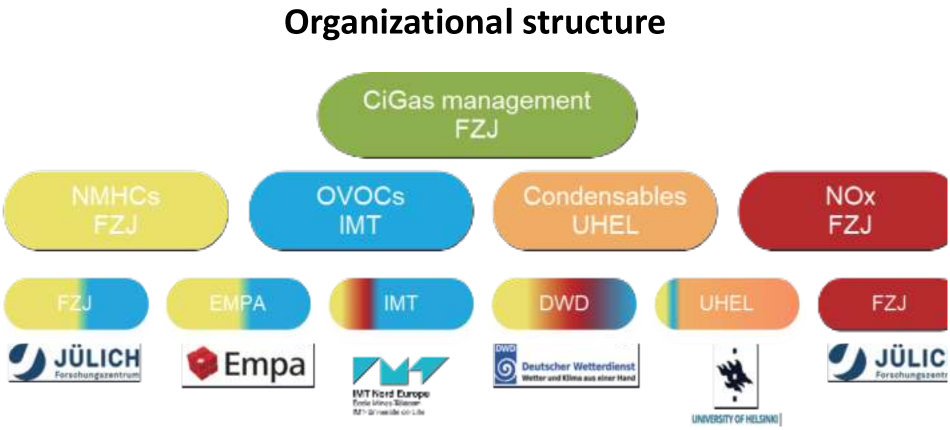

Figure 1: Organizational structure of the Centre for Reactive Trace Gases In Situ Measurements (CiGas).

Experimental Methods

CiGas supports and has capacities in PTR-MS measurements based on Ionicon PTR-Quadrupol-MS, PTR-Time of Flight-MS (e.g. PTR 8000), PTR-Quadrupole ion guide TOF-MS, Kore Technology Ltd PTR-TOF-MS and the Tofwerk VOCUS PTR LTOF MS. Calibrations are performed based on the NPL-20-component gas mixture standard, the IONICON advanced liquid calibration unit, customized standard gases as well as diffusion sources. VOC measurements are complemented by Thermal desorption gas chromatographic on- and offline methods. A FUSION-PTR-LTOF-MS (Ionicon Analytik Ges.m.b.H.) will extend the portfolio of instruments in 2024.

Results

Within ACTRIS 31 observational platforms and 15 exploratory platforms (atmospheric simulation chambers, mobile platforms and laboratories) are operated by European member countries (Fig. 2). For reactive trace gases, in-situ measurements of VOCs and NOx are obligatory at each station. The measurements are harmonized by measurement guidelines for PTR-MS issued by CiGas based on the currently existing instrumentation and literature. The quality assurance and quality control procedures are standardized and mandatory for the currently commercially available instrumentation. The calibrations of instrumentation are traced back on the certified NPL-Standard for PTR-MS. Users are being trained on the instrumentation by dedicated workshops and hands-on trainings. The national facilities are being audited by CiGas on a regular basis and take part in round robin activities as well as inter-comparison campaigns.

PTR-MS data will be freely available reported by a dedicated vocabulary accounting for interferences separated for quadrupole mass spectrometry and high resolution ToF mass spectrometry based on the following concept: “mass <protonated mass> organic compounds amount fraction”, i.e. “mass 107 organic compounds” comprises the sum of benzaldehyde, o-xylene, m-xylene, p-xylene, ethylbenzene whereas “mass 107.086 organic compounds” excludes benzaldehyde from the sum of compounds above. The PTRMS sum parameter are clearly separated from TD-GC-FID/MS data where chromatographic separation followed by mass spectrometric identification of the compounds provide unambiguous compound identification. Data must be reported with the calibration, blank and actual sample measurements to maintain the FAIR principles.

Source Fig : https://www.actris.eu/facilities/national-facilities

Figure 2: ACTRIS Network of National Facilities for Reactive Trace Gas in-situ measurements.

Discussion

Compatibility of VOC measurements from different instrumentation and data producers is an essential factor for users to base their scientific research on reliable data products. The FAIR principle will ensure traceability of the data. The central facilities of ACTRIS in cooperation with the observational and exploratory platforms applying the QA/QC guidelines as being defined by CiGas for reactive trace gas in-situ measurements will ensure a common standard of the data products. Scientific and technological developments are fostered by the consolidated expertise of CiGas in cooperation with industry and the scientific partners. Dissemination of the procedures applied by CiGas is maintained by strong collaborations with other networks, e.g the Global Atmosphere Watch program of the WMO, or the European Committee for Standardization (CEN).

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Applications in Food Science

PTR-MS *in vivo* and *in vitro* measurements of key meat flavor volatile compounds released during consumption of plant-based patties

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Abstract

This presentation will show the utilization of in vivo and in vitro PTR-MS analyses to examine the aroma release of essential meat flavor volatile compounds in plant-based meat analogues. Additionally, a newly developed software is demonstrated to facilitate and streamline the data analysis process.

Introduction

There is an increasing demand of plant-based meat alternatives in the market, where they are gradually moving from being a "niche" product to an everyday food. Despite the growing popularity of plant-based foods, their sensory characteristics is lower compared to animal-based products in terms of texture and flavor [1]. The composition of the so-called meat analogues, such as the type of proteins and fats, significantly influences the flavor. There is a need for deeper knowledge on binding and release of the volatile compounds from meat analogues to guarantee a meaty-like aroma and increase the product acceptance. Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a valuable and versatile analytical approach that can support the investigation of the volatile compound characteristics of the meaty aroma and their release from a plant-based product during consumption. In this presentation will be discussed the applicability of PTR-MS for analysis of in vivo and in vitro aroma release from plant-based patties with added meat flavor volatile compounds. Furthermore, the implementation of a new developed software for a dedicated data analysis will be shown.

Experimental Methods

Samples

24 plant-based patties, with different formulations in terms of fat content, type of fat and protein, were analyzed *in vivo* and *in vitro* using PTR-MS. The same amount of a meaty-like aroma was added to all the samples, containing 6 key aroma compounds of meat. Prior to each measurement, the patties were heated and grilled and 10 grams of sample were sliced for each measurement.

PTR-MS conditions

All measurements were performed using a PTR-QiToF-MS (Ionicon Analytik G.m.b.H., Innsbruck, Austria) to investigate the VOCs. Ionization was carried out under drift tube voltage 999 ± 1 V, drift pressure of 3.80 mbar, temperature 60 °C, and E/N value of 133 Td. Data acquisition was carried out at 1 spectrum per second.

***In vivo* measurements**

The 24 patties were served to 6 participants in duplicate. Physiological parameters (oral cavity, salivary flow, natural eating) were measured for each of the participants. Sampling was carried out by inserting Teflon tubes in both nostrils of the participants. The tubes were part of a heated block (100 °C) connected to the PTR-MS by a PEEK tube (inner diameter=0.5 mm); the Teflon tubes were replaced after each test. At the start of each PTR-MS measurement, laboratory air was sampled for 20 seconds as a baseline. Next, the participant was connected to the PTR-MS by inserting Teflon tubes in each of the nostril, and normal breathing was measured for 30 seconds. After this period, 10 gram of sample was introduced in the participant’s mouth and chewed for 30 seconds at a rate of one chew/second, followed by a swallow. After 30 seconds another swallow was recorded. The second swallow was followed by a post-swallow period of 100 seconds.

***In vitro* measurements: Mouth model**

The 24 patties were measured in duplicate using a mouth model able to mimic the chewing phase. The mouth model was connected to the PTR-MS by a PEEK tube (inner diameter=0.5 mm). At the start of each measurement, the Teflon insert of the mouth model was filled with 1 ml of water to mimic saliva and 10 grams of patty. PTR-MS measurements started with a baseline measurement of 30 seconds of the headspace (no movement of plunger). Then the plunger movements (1Hz horizontal and 1Hz rotational movement) were started for a “chewing” period of 60 seconds. After this, the movements stopped and the PTR-MS measurements continued for a 100 second “post-chewing” period. Then the tube of the mouth model was removed, and a coating was created by pushing the fragmented patty bolus back out of the tube. The tube with the “swallow” coating was connected to the PTR-MS again and measured for 100 seconds with a opposite flow like breathing out.

Results and Discussion

Specialized software was developed to analyze both *in vivo* and *in vitro* data, supporting the visualization and extraction of information necessary for characterizing the release of the aroma compounds added to the samples. The software is able to extract the significant peaks for each sample, and allows the visualization of the sample trends based on parameters such as the area under the curve (AUC), the maximum intensity (Imax), the time maximum (Tmax) for both *in vivo* and *in vitro* analysis next to the slopes of both oral processing and lingering. Additionally, it enables a rapid overview of all participants' *in vivo* release of the meaty-like aroma compounds in the samples, facilitating outliers identification and visualization of interindividual differences. Preliminary results show differences in volatile compounds release among patties with different fat content (6% and 14 % fat). Specifically, similar results were observed for the *in vivo* and *in vitro* analysis for 3-methylbutanal and 2,3-pentanedione. These results demonstrate the potential of the application to study the release of volatile compounds of plant-based patties with different formulations both *in vivo* and *in vitro* making use of a mouth model. The software developed for data analysis shortened the data analyses and provides fast insight in the oral processing and aroma release. Moreover, these *in vivo* and *in vitro* PTR-MS measurements can be used for optimize flavoring and therefore improving acceptability of plant-based products.

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Harnessing the versatility of PTR-MS to explore the multifaceted world of food volatiles

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Abstract

When PTR-MS was developed almost three decades ago, it steadily found footing in applications relating to food/flavor analysis, alongside its more prominent rise to fame in the atmospheric chemistry community. The ability for volatile food aroma or spoilage compounds to be detected directly in the gas phase with real-time resolution made PTR-MS the ideal tool for non-destructive, high-throughput screening or continuous monitoring of dynamic processes, previously unachievable with conventional analysis using GC-MS. This talk will review the early explorations of PTR-MS in food analysis, its subsequent implementation to a broader range of applications, and will highlight key developments that have positioned PTR-MS as a competitive technology in the area of food volatiles analysis.

Introduction

The 1995 paper by Hansel and colleagues that introduced the world to the technique of PTR-MS, as well as the 1998 follow-up paper in Chemical Society Reviews by Lindinger, Hansel and Jordan, reported proof-of-principle analyses for several applications, yet food analysis was only marginally featured. The companion seminal 1998 paper by the same authors, however, included a subsection on food applications that showcased early studies on fruit ripening, coffee roasting, and meat spoilage [1]. Subsequently, individual research papers exploring the use of PTR-MS in food science began to emerge through collaborations of the Innsbruck team with the Nestlé Research Center in Switzerland and the Agricultural Institute in Italy, spearheaded by Yeretzian and Biasioli, respectively. Early applications had a strong focus on coffee, ranging from green beans to the roasting and brewing processes, but also covered topics that included ripening, maturation and screening of fruits and dairy products (as reviewed in [2]). A steady output of papers featuring PTR-MS-based studies followed, and the technique gradually gained popularity through its analytical capabilities that complemented existing flavor analysis based on GC-MS.

Discussion

Despite still being a niche technique compared to GC-MS – and being greatly overshadowed by the latter in terms of the number of instruments in operation – PTR-MS is a force to be reckoned with in food science due to its unique analytical capabilities. From the early explorations that were accompanied by a handful of research articles published per year, papers in the scientific literature that report on the use of PTR-MS in the area of food-flavor analysis now number around 30 on average per year. To date, almost 500 articles featuring food-related topics have been published (see figure 1), according to a recent search on SCOPUS.

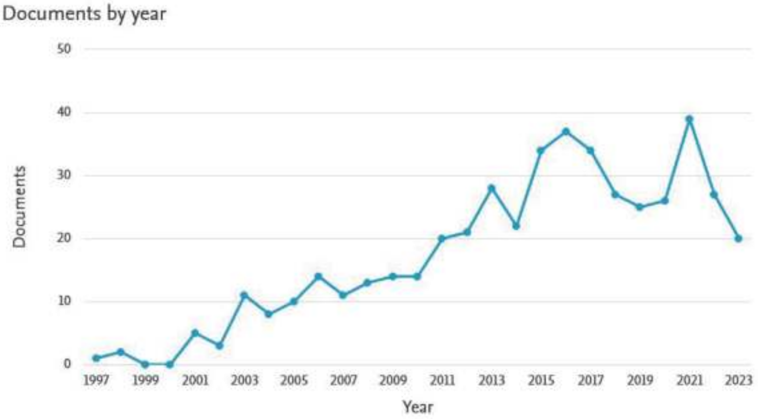

Figure 1: The steady rise of PTR-MS articles in the literature focusing on food research (search and output via SCOPUS)

Beyond the initial and more intuitive uses of PTR-MS mentioned above, several innovative food-flavor applications have been reported over the years. These have included the coupling of PTR-MS to model mouth systems to examine food oral processing under controlled conditions, interfacing it to espresso coffee machines to characterize aroma extraction kinetics during brewing, headspace analysis of coffees to predict sensory profiles, and connection to a nasal catheter to examine odor perception.

In recent years, peripheral equipment has been developed that greatly expands the possibilities for implementing PTR-MS. The fast-GC interface, for example, makes it possible to separate isomers – to a degree – in complex sample matrices containing diverse flavor compounds, whilst simultaneously allowing for the analysis of alcoholic beverages due to the early elution of ethanol that can be discarded from the analysis and thereby not deplete the primary ions and disrupt the ion chemistry in the drift tube [3]. Another major advancement was the connection and optimization of PTR-MS to an autosampler system, allowing for rapid analysis of multiple samples in succession to achieve high-throughput headspace analysis [4]. Further progress has been made through the development of the liquid calibration unit (LCU), not only to allow for the calibration of PTR-MS for aroma compounds via bespoke mixtures, but also as novel delivery system for liquid samples. In the latter constellation, supplying the LCU with the beverage sample enables direct analysis of constituent aromas by PTR-MS via the gas-phase after nebulization, as has been demonstrated for whisky [5] and coffee (see abstract by Cleve *et al.*). A recent development, albeit not yet applied in food-flavor studies, has been the connection of the PTR-MS with a commercial micro-chamber/thermal extractor (µCTE) device that enables the volatile emissions from small samples to be analyzed in real-time under defined conditions of temperature and chamber volume exchange [6] (see also abstract by Beauchamp and Pham). This has been demonstrated hitherto on the emissions from polymer materials, but is equally applicable to food samples.

Conclusion

PTR-MS can be considered well-positioned in food-flavor research as a powerful analytical tool that complements conventional analyses of aroma or odor-active compounds via GC-MS [7, 8]. Its implementation in this field over the past decades has led to many insights and discoveries for a broad range of topics in food chemistry, from microbial spoilage, fermentation and maturation, and oxidative degradation, to aroma stability, generation via food processing, and sensory perception. No doubt, PTR-MS will remain an essential tool in future undertakings to explore food in relation to volatile constituents, both desired and undesired.

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Understanding the *in vivo* flavour release and perception of plant-based meat analogues in relation to their structural properties by using proton transfer reaction-mass spectrometry.

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Introduction

Food security could be assured for future generations if humanity shifts from animal-based diets to more plant-based diets [5, 8, 9]. Plant-based meat analogues (PBMAs) have the potential to assist consumers in making dietary changes and accelerate the protein transition. However, the palatability of the currently available PBMAs is not yet at the same level as the meat products that they try to replace. The mechanisms behind flavour formation, flavour release and perception, and the impact of textural attributes on meat palatability are known and well-described [1, 2, 3, 4, 6, 7, 10]. In contrast to meat, little is known about flavour formation, flavour release and perception, and the impact of structure and texture on consumer acceptance of PBMAs. These mechanisms and their interactions must be better understood to improve the overall quality of PBMAs. The current project aims to determine how differences in structural and textural properties affect oral structural breakdown and consequently the *in vivo* flavour release and perception of PBMAs. The objective of this study was to determine how serum release and juiciness of PBMAs affect *in vivo* flavour release and perception.

Methods

Burger patties were made from PBMA mince and spiked with menthone (0.01 w/w%, $M_w = 154$ g/mol, log $P = 2.7$). Internal cooking temperature (60, 70, 80 and 90°C) of the PBMAs was varied during preparation. A naive consumer panel (n=99) evaluated all PBMAs using Rate-All-That-Apply methodology. As internal cooking temperature decreased from 90 to 60°C, the serum release under compression and juiciness intensity of PBMAs significantly ($p<0.05$) increased. With increasing juiciness of PBMAs, fattiness and chewiness increased, while dryness decreased significantly ($p<0.05$). Juiciness was significantly positively correlated ($p<0.05$) to the amount of serum released under uniaxial mechanical compression, and serum composition. Serum release under compression was related to serum release under oral conditions.

Results & Discussion

Once juiciness differences between the PBMAs were confirmed, we investigated the effect of serum release on *in vivo* flavour release and perception. *In vivo* nose space Proton Transfer Reaction Mass Spectrometry was used to monitor the release of menthone over time while simultaneously aroma intensity (*i.e.* peppermint) was quantified using Time-Intensity sensory profiling (n=13, triplicate). *In vivo* menthone release during mastication was affected by serum release and juiciness and impacted dynamic peppermint perception suggesting that increased serum release increased aroma release and perception. We conclude that serum release and juiciness of plant-based meat analogues impact *in vivo* aroma release and perception.

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Green analytical approaches and sustainable transition of food systems: the potential of PTR-MS to speed up innovation in fermentation

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Abstract

An important part of the foods produced and consumed are fermented foods. Improving and optimizing the contribution of fermentative bioprocesses means promoting the transition of food systems towards increased standards of environmental, social and economic sustainability. The Proton transfer reaction-mass spectrometry, with its analytical potential and compliance with the guidelines for 'green' analysis in the monitoring of volatile organic compounds, represents a highly interesting tool for promoting innovation in the fermented food and beverage sector. The review proposes a series of case studies to explore the potential and future prospects.

Introduction

A third of the foods we eat are fermented products, a heritage of millennia of transformation of raw materials with a low energy footprint and with good potential to improve shelf-life, sensorial, nutritional, functional quality and food safety [1, 2], promoting the development of desired microorganisms, as pro-technological, probiotic and/or biocontrol agents [3]. Fermentations have thus given rise to a large part of the 'glocal' food and wine heritage and are today rediscovered for their significant contribution to the green transition of agri-food systems. Of particular interest is the synergy between environmental, social and economic sustainability [1]. In fact, fermenting in a rigorous and controlled manner means reducing energy and synthetic chemical inputs in food processing, enhancing microbial diversity, promoting the reuse of by-products and waste, improving quality and safety, supporting important industrial sectors (food and beverages, microbial biotechnology), promoting innovation in these sectors. The fact that it is estimated that there are more than 5000 different fermented products worldwide diffused [4, 5] provides a good idea about the number of variables that need to be evaluated in the study and improvement of food/beverage quality and safety, development of new products and, more generally, promoting innovation in the food sector. If we then add changes in consumer lifestyles, hedonic trends, the importance of personalized nutrition and functionality, scientific discoveries in the field and the importance of facing global changes, the interest in green, versatile and cost-effective analytical strategies capable of speeding up innovation in the fermented foods and beverages field is becoming clearer and clearer.

Experimental Methods

The experimental methods followed foresaw the adoption of appropriate searching strategies in the scientific literature databases to perform a narrative review on the potential of PTR-MS to speed up innovation in the fermentation of foods and beverages.

Results and Discussion

Microorganisms, with their metabolism in foods, produce volatile organic compounds (VOCs) [6]; at the same time, volatile molecules are important because they provide us with integrated information on quality and safety [7, 8]. From this point of view, VOCs represent interesting analytical targets for rapid monitoring and massive screening in the fermentation field. Proton transfer reaction-mass spectrometry (PTR-MS) allowed rapid and direct measurements of VOCs, assuring very informative analytical data [6, 7]. The combination of PTR-MS with an autosampler and a tailored data analysis has enhanced the degree of automation and versatility in use, supporting exploitation similar to a sensor approach. The overview of case studies proposed aims to underline the versatility of the PTR-based approach in the study and monitoring of fermentation processes using VOCs as markers of relevant phenomena in a holistic vision of transformations, quality and safety [9], promoting sustainable innovation. The diversity of the variables explored includes the assessment of different categories of fermented matrices (e.g. bread, wine, beer, dairy [10-13] the evaluation of different microorganisms of interest in food bioprocesses (i.e. bacteria, yeasts and filamentous fungi) [11, 13], the study of the main fermentative processes (e.g. alcoholic fermentation and lactic fermentation) [11, 13], the evaluation of other non-fermentative processes [14, 15], the interaction between microorganisms [13, 16] and raw materials and the interactions between microorganisms [13, 17]. The narrative review also encompassed the recent outputs from ongoing research activities supported by the projects ‘iNEST’, ‘ONFOODS’ and ‘AGRITECH’ [Italian National Recovery and Resilience Plan (NRRP) projects financed by the European Commission’s Next Generation EU programme]. Alongside a detailed discussion of future prospects, the overview underlines the 'green' character of the PTR approach [8], which concretise an interesting synergy between green analytical approaches for research and development and the sustainable transition of food systems through the promotion of the benefits associated with fermentation processes.

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Insights into aroma extraction during coffee brewing using a coupled LCU-PTR-TOFMS approach

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Abstract

Espresso coffee extraction is a complex process regulated through different interdependent parameters, such as water flow rate and extraction pressure, coffee particle size, and extraction time and temperature. An evaluation of the influence of these parameters on the extraction kinetics of coffee aroma compounds over a wide range of settings entails a high number of samples with lengthy analyses. In this study, a liquid calibration unit (LCU) was used to vaporise filtered coffee extracts for direct and rapid quantitation of selected aroma constituents using proton transfer reaction time-of-flight mass spectrometry (PTR-TOFMS). The extracted quantities of aroma compounds were observed to decay exponentially with extraction volume. The degree of extraction varied mostly in relation to the volatility and polarity of the individual compounds, whereas the extraction parameters had only a minor influence. A brewing temperature of 98 °C led to a higher extraction of less polar compounds, like 2,3-diethyl-5-methylpyrazine, 2-isobutyl-3-methoxypyrazine, vanillin, and linalool. The lowest extraction flow rate (1 mL/s) led to slightly higher abundances of aroma compounds in the coffee, while no such effect was observed in relation to particle size. This novel approach to quantify aroma constituents directly in the liquid phase via gas-phase analysis using the LCU was validated in terms of the limits of detection and quantitation (LOD and LOQ, respectively), repeatability, method precision, and accuracy. The validation showed good precisions (<6 % and <10 %, respectively) and low LODs and LOQs (31−983 $\mathrm{ppt_V}$ and 0.1−3.2 $\mathrm{ppb_V}$, respectively), although the method accuracy was rather low, with recovery rates ranging between 32 % and127 % for the analysed compounds, depending on their physicochemical properties.

Introduction

Coffee is one of the most consumed beverages worldwide, enjoyed for its complex flavour, stimulating properties, but also the social aspects associated with its consumption. Coffee flavour is influenced throughout the whole processing chain, starting with the crop selection and ending with coffee brewing and serving [1]. There are various methods to brew a coffee (e.g., drip brew coffee, French press coffee, or espresso coffee) and these can be regulated by adjusting different parameters, such as the grind size of coffee beans, brewing temperature, extraction time and flow rate, as well as the extraction pressure for some methods. Espresso coffee extraction utilises high extraction pressures (~9 bar) and short extraction times (~25−30 s) to create small volumes of intense coffees.

Although espresso coffees have been studied extensively over the last years, most investigations implement offline analysis and only two studies to date have investigated the extraction kinetics of coffee aroma compounds by implementing headspace analysis of the emerging brew using proton transfer reaction-mass spectrometry (PTR-MS) [2, 3]. Characterisation of the extraction kinetics via off-line approaches requires the collection of several samples for each extraction process, with the samples conventionally analysed using gas chromatography (GC-MS), mostly using solid-phase microextraction (SPME) involving lengthy analysis times [4].

The aim of this study was to assess the suitability of PTR-time-of-flight-MS (PTR-TOFMS) for high sample-throughput analysis by direct evaporation of the coffee extracts using an LCU. This novel approach was used to evaluate the influence of grind size, water temperature and flow rate on the extraction kinetics of selected aroma compounds during espresso coffee extraction.

Experimental Methods

The influence of temperature (80, 89, 98 °C), flow rate (1, 2, 3 mL/s) and grind size (settings 0.8, 1.4, 2.0) was evaluated by varying one parameter at a time whilst keeping the other two at the intermediate settings. The workflow shown in *Figure 1* was applied for the sample analysis. Double espresso coffees (60 mL) were prepared in triplicate using 20 g freshly ground, medium roasted Arabica coffee.

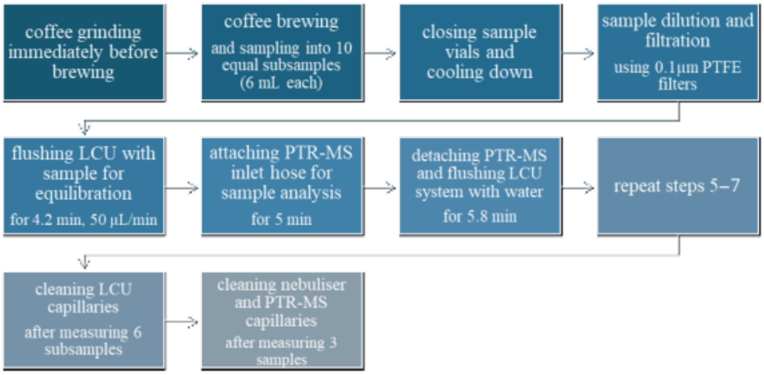

Figure 1: Sample analysis workflow

The analytical method was assessed in relation to LOD/LOQ, repeatability (n=6, subsample 1 of coffee brewed at intermediate settings), method precision (n=5, over 5 days, subsample 1 of coffee brewed at intermediate settings, freshly prepared each day), and accuracy (standard addition, mixing coffee with a standard reference mixture using both pumps of the LCU).

Results and Discussion

Extraction kinetics of coffee aroma compounds

The extraction kinetics of the individual aroma compounds in the coffee were calculated as their concentrations in the individual subsamples in relation to the accumulated volume of the espresso coffee brew. The highest concentrations were detected in the first subsamples (initial extraction volume), with an exponential decay in concentrations over the total extraction process [5], as is consistent with previous studies [2, 3]. The form of the extraction curves was compound-dependent: more volatile and polar compounds showed a steep decay, while less volatile and polar compounds followed a flatter, almost linear trend [5]. This is observable in the raw data, plotted on a logarithmic scale in *Figure 2*. The dependency of extraction on the compound’s polarity has been described in the literature and is explained by the better solubility of polar compounds. This leads to faster extraction and a sharper decrease in concentration over time than for less polar compounds, which are extracted more slowly and therefore over a longer period [6].

The influence of brewing parameters was especially noticeable for less polar compounds, such as 2,3-diethyl-5-methylpyrazine and vanillin. The highest temperature (98 °C) led to higher concentrations in the first subsamples, yet there were no significant differences due to variations in grind size. The flow rate of 1 mL/s yielded slightly higher aroma concentrations with a significant effect for 2-methoxyphenol and 2-acetylpyridine. Overall, differences in aroma composition were minor [5].

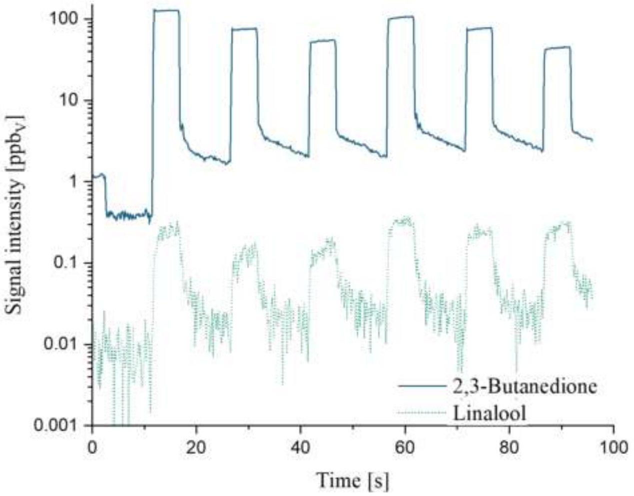

Figure 2: Signal intensity of linalool (lower trace) and 2,3-butanedione (upper trace) during analysis of subsamples 1, 2, 3, 5, 7, and 10 of an espresso coffee brewed with medium settings (89 °C, 2 mL/s, grind size 1.4). Note that the dilution of subsamples 1−3 was higher compared to subsample 5, 7 and 10.

Method validity

The LOQs were determined to range between 3.2 and 0.1 ppb$_V$, with corresponding LOD values between 31 and 983 ppt$_V$. The precision of repeatability, as determined by the relative standard deviation of six consecutive measurements of the same sample, was below 6 %. The analysis of the first subsample of a daily brewed coffee using the same extraction parameters resulted in a standard deviation below 10 %, indicating good repeatability of the method. Method accuracy was determined by standard addition. A coffee sample with known concentrations of aroma compounds was mixed with a reference mixture through use of the second micropump of the LCU, whereby the reference solution was added at the same rate as the standard coffee; mixing was thereby achieved in the final capillary before injection into the LCU evaporation chamber via the nozzle of the nebulizer. Recovery rates of the standard references was 80−120 % for eight compounds but overall 32−127 % due to poor mixing/recovery of some compounds. This comparatively low accuracy might be attributable to inhomogeneous mixing of the two liquids in the LCU, or explained by the complexity of the coffee aroma and limited selectivity of PTR-TOFMS compared to GC-MS methods, leading to an overlap of compounds. Moreover, the complex coffee matrix, which includes melanoidins, polysaccharides and acids, amongst others, could act to retain aroma compounds. During clean-up, brown sediments were found within the LCU tube and the capillaries of the PTR-TOFMS inlet system [5].

Conclusion

Overall, the effect of varying extraction parameters on the extraction of aroma compounds was low within the ranges applied in this study; this was confirmed by sensory analyses, whereby differences in coffee extracts were barely noticeable. In terms of the analytical procedure, the presented method successfully demonstrated a high sample throughput and low sample workup compared to conventional GC-MS analysis. Furthermore, the precision was good, with low LOQs and LODs, enabling a reliable relative comparison of samples; the accuracy was rather low for some compounds, but is potentially improvable, for instance, by optimising the method but also for less complex beverages. One downside of the method was the frequent and time-consuming cleaning required due to aggregation of coffee melanoidins within the system.

Acknowledgements

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Exploring the impact of dietary substrates on the gut volatilome: non-invasive *in-vitro* VOCs monitoring

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Introduction

Intestinal fermentation is a complex process with major consequences for human health as it produces chemicals that might affect host well-being [1]. The present investigations in human gastrointestinal metabolomics primarily concentrate on conventional metabolomes, overlooking to account for volatile organic compounds (VOCs) [2]. Metabolomics is often characterized by static sampling and prolonged analysis times, neither of which permit the investigation of temporal dynamics in microbiome studies [2,3]. Direct injection - Mass Spectrometry (DI-MS), enables the investigation of metabolic processes in real-time [2,3]. Examining the potential applicability of DI-MS, this work aims to highlight VOCs potential as non-invasive biomarkers and their potential to address new challenges in gut microbiome research.

Experimental Methods

In this study we compare two fully automated methodologies, namely headspace solid phase micro extraction coupled with gas chromatography-mass spectrometry (HS-SPME-GC-MS) and statistic headspace module coupled with proton transfer reaction coupled with time-of-flight mass spectrometry (SHS-PTR-ToF-MS) to capture the gut volatilome in-vitro. The objective is to establish a synergy between GC-MS profiling capabilities and PTR-ToF-MS high throughput quantitative monitoring to elucidate VOCs changes in composition and concentration throughout batch fermentation model systems. We examined VOCs longitudinally throughout colonic fermentation experiments with in-vitro digested dietary substrates (e.g. oat bran). The datasets were firstly explored by principal component analysis (PCA). Furthermore, we employed the ANOVA Simultaneous Component Analysis (ASCA+) which combines conventional linear models with PCA, enabling the decomposition and visualization of the individual impacts of experimental components [4] such as fermentation time, substrate tested and donors. The workflow is also presented in Figure 1.

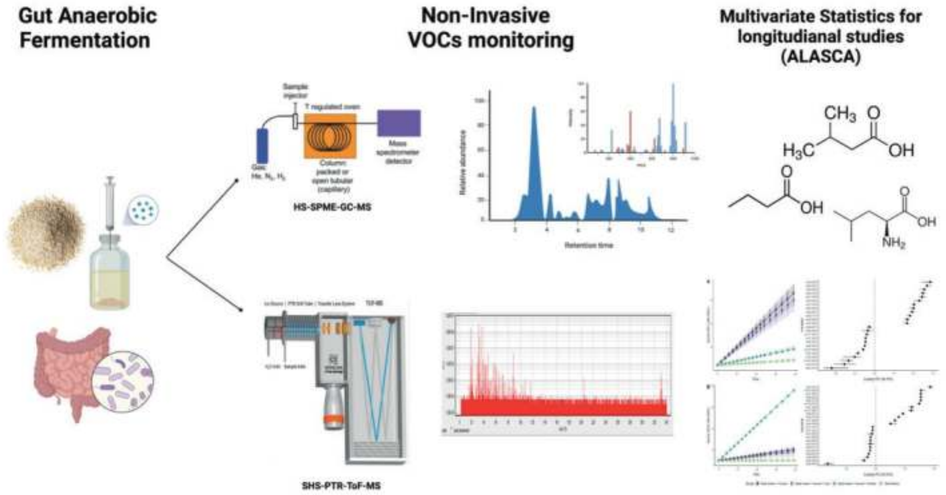

Figure 1: Non-invasive VOCs monitoring coupled with multivariate statistics for longitudinal studies is suited for the assessment of metabolic events taking place during gut microbial batch fermentation model systems.

Results and Discussion

HS-SPME-GC-MS and SHS-PTR-ToF-MS were used to evaluate oat bran anaerobic in-vitro fermentation performed directly in nitrogen filled 20mL vials [5,6]. The two approaches were successful in detecting the time of release of numerous classes of molecules.

The GC-MS method detected short chain fatty acids (SCFAs) and medium chain fatty acids (MCFAs) generated by oat bran fermentation after 8 hours. Several sulphury reactive metabolites, such as thiophenes, were also found in the microbial headspace. PTR-ToF-MS was also capable to monitor the emission of SCFAs and MCFAs, even though with less capabilities to elucidate structural isomers. By contrast it was capable to highlight unique differences in sulphur metabolism by tracking important compounds like methanethiol and hydrogen sulfide.

Overall, the described methodologies were both needed for the evaluation of real-time changes in small metabolites occurring over various temporal events during the batch fermentation process. Our findings reveal how the headspace in a colonic batch fermentation model is far more dynamic, with multiple different processes taking place during fermentation. The observed temporal fluctuations are characterized by distinct events, emphasizing the importance of streamlining sampling and analysis using high throughput methodologies. Therefore, despite its analytical limitations, we leverage PTR-ToF-MS as a robust and novel method to capture the gut volatilome in-vitro and address new challenge in gastrointestinal research.

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PTR-MS and gas sensors: a mutualistic relationship

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Abstract

The chemical analysis of gaseous samples is undeniably pivotal in numerous scientific and industrial arenas, including but not limited to food analysis, environmental control, and medical diagnosis. In these diverse fields, the ability to identify specific patterns of volatile compounds plays a crucial role in uncovering essential information about the properties of food, responding to environmental emergencies, and diagnosing various medical conditions. Consequently, a substantial amount of research and development efforts are dedicated to advancing analytical instrumentation capable of swiftly and reliably providing insights into the unique patterns of volatile compounds characterizing different types of samples.

Direct injection mass spectrometers, with PTR-MS being a notable example, emerge as a highly promising solution owing to their impressive sensitivity, selectivity, and rapid measurement capabilities. However, the widespread adoption of these instruments in routine applications is hindered by challenges such as their inherent complexity, size, and relatively high cost. In contrast, the realm of sensor technology holds great promise in the creation of devices that are not only sensitive to the chemical composition of gaseous samples but are also sufficiently simple to be seamlessly integrated into electronic circuits. The prevalence of micro-electromechanical systems in common devices like smartphones stands as a testament to the advancements in sensor capabilities and their potential for widespread applications.

Yet, despite the advantages offered by sensors in terms of reduced size, cost-effectiveness, and integrability with microelectronic platforms, there exists a general trade-off with respect to sensitivity and selectivity.

Acknowledging that both PTR-MS and gas sensors operate in real-time, a recent and innovative approach proposes the amalgamation of these instruments. By combining the strengths of PTR-MS and gas sensors, we aim at optimizing the overall performance of the sensor systems in specific applications. This hybrid methodology is particularly promising as the signals from mass spectrometers serve as a valuable reference, facilitating the definition of optimal feature extraction from sensor signals.

Illustrating this innovative concept, the combination of PTR-MS-ToF and a gas sensor array, comprised of quartz microbalances coated with molecular films of metal complexes of porphyrinoids [1], has been applied. Two compelling case studies further elucidate the potential of this hybrid approach: the examination of the volatilome evolution of Plasmodium falciparum-infected erythrocytes [2] and the analysis of changes in volatile compounds in tomato pastes treated with natural antibacterials [3].

These case studies not only underscore the feasibility of integrating PTR-MS-ToF and gas sensors but also shed light on the practical benefits derived from this symbiotic relationship. In the analysis of tomato paste the comparative examination reveals intriguing insights into the temporal dynamics of sensor signals, influencing the accuracy of class identification by the sensor array. The comparison of sensors signals with those of PTR-MS demonstrated that most of the relevant information in sensors signal is achieved in the very first instants of the exposure. This findings is leading to a better optimization of sensors experimental design and, since sensors are exposed to smaller amount of samples, in a longer sensors lifetime.

Similarly, in the investigation of Plasmodium falciparum, PTR-MS-ToF evidenced hexanal as a distinctive marker indicative of the transition between the asexual and sexual stages of the parasite's lifecycle. This crucial information not only enhances our understanding of biological processes but also guides the refinement of sensor arrays, ensuring a balance between cross-selectivity and heightened sensitivity, particularly towards hexanal.

In essence, the integration of PTR-MS with gas sensors represents a cutting-edge approach with far-reaching implications. Beyond providing a comprehensive characterization of the chemistry underlying specific problems, this hybrid methodology actively contributes to the strategic development and optimal operation of gas sensors, fostering advancements in diverse scientific and industrial applications.

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Evaluate, understand and create agri-food biodiversity. Direct injection mass spectrometry can help us!

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Abstract

Agri-food biodiversity is vital for resilient crops, food quality, and sustainable farming. Assessing and understanding this diversity is crucial. Genetic analysis improves plant resilience, nutrition, and fruit quality, requiring precise characterizations using advanced methods. Volatile organic compounds (VOCs) offer insights into fruit health and quality, but limited evaluation methods hinder their study. PTR-MS-based VOC phenotyping emerges as a potential solution. Our institute integrates these approaches into the breeding selection of the main fruit crops. We start by evaluating genetic variability in germplasm collections, revealing hidden traits crucial for resilient fruits. Genetic studies, like GWAS and QTL analysis, uncover genes and pathways linked to VOCs, influencing fruit aroma and quality. Leveraging this genetic insight, we pioneer breeding programs, creating fruits resilient to stress with enhanced aroma and flavor. In addition, understanding plant-microbe interdependence, influenced by VOCs, drives sustainable practices, and enriches flavors through microbial diversity.

Introduction

In agriculture, the agri-food biodiversity plays a critical role in fostering resilient crops, enhancing food quality, and promoting sustainable farming methods. This underscores the essential need for a comprehensive assessment, understanding, and cultivation of this biodiversity.

Objective, detailed analysis of interspecies genetic-phenotypic diversity is essential for promoting new biological diversity. This involves genetic improvement plans targeting plant resilience against stressors, enhancing nutraceutical attributes, and improving fruit quality. Achieving this, demands precise integration of morphophysiological and biochemical plant and fruit characterizations, utilizing synergistic multi-omics and high-throughput methodologies.

Volatile organic compounds (VOCs) in agri-food products have gained significant scientific attention. VOCs act as bio-signatures revealing the physiological and biochemical status of fruits [1]. Their analysis not only aids in comprehending the impact of environmental stresses on plants but also sheds light on the quality attributes of fruits that are essential for both growers and consumers. However, the so called "phenotyping bottleneck", caused by the absence of high-throughput and non-invasive methodologies, impedes an effective evaluation and prediction of food and plant VOCs [2]. These new peculiarities have therefore required the need to make available analytical techniques that are rapid, applicable even without the need for laborious chemical preparation and/or extraction, and reliable. Many studies, carried out in the last decade, have shown that PTR-ToF-MS may be the ideal instrument for this type of studies [3].

This presentation aims at supporting the development of efficient fruit VOC phenotyping methodologies, based on PTR-MS technology, suitable to address the aroma complexity of agri-food products in different situations. In our institute, this synergism of novel analytical approaches is fully applied into the breeding activities of several fruit species (i.e. blueberry, raspberry, strawberry, apple, and grape).

Results and discussion

Germplasm evaluation

Our research journey begins by evaluating the genetic variability inherent in germplasm collections [4, 5, 6, 7]. Each collection embodies a wealth of genetic diversity waiting to be explored. Through advanced VOC analysis techniques, we can decipher the intricate spectrum of VOCs emitted by diverse germplasms, unearthing hidden traits and characteristics crucial for breeding resilient and high-quality fruits.

Genetic association studies

To delve deeper into the genetic underpinnings of VOC production, genetic association studies are conducted [6, 8, 9]. Genome-Wide Association Studies (GWAS) and Quantitative Trait Loci (QTLs) analysis serve as our guiding tools, supporting the identification of genes and metabolic pathways linked to VOC production. This understanding allows us to unravel the genetic overriding aroma and quality traits in fruits.

Breeding activity

Using insights from genetic studies, we initiate pioneering breeding programs to harness novel genetic variability [4, 5]. This integration enables the development of fruit varieties with improved aroma, flavor, and stress resilience. By crossbreeding and selecting for targeted VOC profiles, we cultivate fruits meeting market demands while thriving in diverse environments.

Role of microbiological biodiversity

Recognizing the interdependence of plants and microbes, often actively regulated by VOCs, we explore microbiological variability [10, 11]. Microorganisms profoundly impact plant growth, hormone regulation, and stress resistance. Harnessing this diversity drives sustainable agronomic practices, fostering robust crops. In food studies, microbial variability, notably on fruits, shapes fermentation, enhancing flavors and textures. Leveraging this diversity enriches food preservation and creates distinct culinary experiences, celebrating agri-food biodiversity.

Conclusion

By evaluating genetic and microbiological variability, coupled with innovative breeding programs, and tailored pre- and post-harvested studies, we unveil the untapped potential within the realms of agri-food biodiversity. This holistic approach may help to fortify crop resilience and fruit quality and storability. Our studies confirmed the potentials of PTR-ToF-MS application into the whole agro-food production chain, from breeding to consumers. In addition, these studies allowed to estimate the interaction between genetic variability, ripening stages and storage condition on the quality of several fruit species. Another important achievement was the development of putative VOC and molecular markers linked with fruit organoleptic quality and fruit spoilage caused, for instance, by the occurrence of abiotic and biotic disorders.

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Volatile compound monitoring to support food products design: the role of PTR-MS

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Abstract

The rapid detection of volatile compounds is a precious tool in the design of innovative food products, also combined with the traditional gas chromatography analysis. In the last few years, the PTR-MS has been used in multiple applications, taking advantage of its peculiar characteristics. The use of PTR-MS in quality control of the food ingredients is the most traditional application: the high throughput early detection of target markers of sensory defect can be done at high sensitivity. In this respect, many examples have been proposed and the efficiency of PTR-MS in respect to other techniques has been largely discussed [1].

The possibility of monitoring the real time volatile release in the nasal cavities opened several possibilities for the food designers. The interaction of the volatile compounds with the food matrix is a key factor influencing the food experience not only before the food ingestion, but also during the mastication time. The aroma released in the oral cavity can be monitored by putting two Teflon tubes connected to the PTRMS in the nostrils to monitor real time the in-nose space during the food consumption experience.

In this way we monitored the release of defined volatiles such as menthol and menthone during chewing gum mastication: data showed that the concentrations of these compounds in the nose are proportional to their sensorial perception. In the same study, we also observed that saliva plays a key role in the release of the volatile compounds present in the food product [2].

The real-time monitoring of the specific interaction between proteins and volatile is particularly relevant in the meat analogues design where the formulation of the aroma and its release during the consumption is the key factor influencing consumer’s acceptance. During this lecture the more recent applications of PTR-MS to guide and support decision in formulation and processing will be illustrated.

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How not to get your PTR-TOF drunk: automated targeted and untargeted headspace analysis of spirits

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Abstract

After a general review of what has been published about the different strategies on proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) usage in the case of alcoholic beverages, we present a recent development in conjunction with a multipurpose head-space automated sampler employing Argon as a buffer gas in the static head space module. The aim was to investigate the volatile organic compound (VOC) profiles of 32 different alcoholic beverages. Additionally, the study involved the evaluation and quantification of methanol content in these drinks. This was achieved through the calibration of methanol in the presence of three different concentrations of ethanol.

Introduction

Alcoholic beverages are drinks containing ethanol, which is produced by fermenting different sources of sugars, in some cases with the addition of fruit and herbal infusions. Among alcoholic beverages, spirits result from distillation and therefore have a higher ethanol content. The aromatic component of liquors is widely appreciated by consumers and is a subject of studies in food science. Furthermore, for safety reasons legal limits are established for some naturally occurring or added compounds like methanol.

PTR-ToF-MS as a part of direct injection techniques is a powerful tool to measure VOCs emitted from the different food matrices. However, the high ethanol content present in alcoholic beverages is an issue for PTR-MS since its primary ion could be nearly depleted in the normal working conditions of the instrument. Over the last two decades, this subject has been investigated by many researchers who suggested 6 possible strategies to overcome this problem: i) ethanol saturation, ii) sample dilution, iii) Argon as buffer gas, iv) high E/N, v) coupling PTR-ToF-MS with a fastGC inlet system, vi) coupling PTR-ToF-MS with a liquid calibration unit [1, 2].

In this contribution, after reviewing the strategies adopted so far, we test the use of Argon as buffer gas to evaluate VOCs content of different types and origins of grappa, tequila, mezcal, gin, and other without any sample dilution. Moreover, special attention is paid to evaluate and quantify the methanol content in these distilled drinks.

Experimental Methods

The setup for this study was a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) coupled to a multipurpose head-space automated sampler (Gerstel GmbH, Mulheim am Ruhr, Germany) and a SHS module. The drift tube conditions were as follows: 110 °C drift tube temperature, 2.8 mbar drift pressure, 628 V drift voltage. This led to an E/N ratio of about 140 Townsend (Td). The inlet and SHS module were heated at 110°C as well. The flow of 90 sccm of pure Argon was applied through the SHS module. This approximately resulted in a 10-fold decrease of m/z 21.022 signal and 1000 time of water cluster of m/z 55.039 one. The acquisition rate was set to 1 spectrum/s.

32 different liquors such as grappa, brandy, gin, mezcal, tequila were analyzed.

Standard solutions for methanol quantification were prepared by dissolving methanol at different concentrations (0-0.3 mL) in three different hydro-alcoholic solutions (60/40, 50/50, and 60/40 water/ethanol ratio, in volume). 5 μL of each sample were transferred into a 20 mL vial. Samples at each concentration level were in prepared in triplicate. Samples were kept at 10°C prior the analysis and then incubated for 10 min at 40°C. 2.5 mL of sample headspace were taken and injected into SHS module at the speed of 50 μL/s.

Deadtime correction, internal calibration of mass spectral data, and peak extraction were performed according to previously described procedures [3].

Results and discussion

362 mass peaks were extracted from the raw data. 36 ethanol-derived ions (isopologues, fragments and clusters) and 9 methanol-derived ones were observed in the mass spectral data.

The method applied in this study allowed to measure the alcoholic beverages from 14 to 95.99% of ethanol without any setup change. It was possible to quantify methanol as an important contaminant of distilled spirits and compared with the calibration curve of methanol in the range from 0 to 3% in different percentages of ethanol – water solutions. The negative effect of ethanol on the quantification of methanol was observed especially for the solution of 60% of ethanol.

The univariate and multivariate PLS-R models were built for the prediction of methanol and/or ethanol content prediction. Moreover, PLS-DA model was built to distinguish different classes of liquors.

Conclusions

Despite high ethanol concentrations limiting the PTR-MS performance, it is still possible to obtain valuable insights also in the case of alcoholic beverages. These insights can be relevant for quality control or monitoring fermentation/distillation processes. In particular, it has been demonstrated that robust classification systems can be developed for some of the major alcoholic beverages. Furthermore, a rapid and non-invasive estimation of methanol content, a crucial safety component in these products, can be achieved.

This study highlights the effective utilization of PTR-MS even in suboptimal conditions characterized by high ethanol content.

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Influence of hydrolysis method, lactase purity and temperature on Maillard reactions in lactose-hydrolysed UHT milk

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Abstract

To serve lactose intolerant consumers worldwide, dairy producers need long shelf-life milk to be able to ship it over long distances at ambient temperature. While ultra-high-temperature (UHT) treatment can increase conventional milk shelf life up to 9 months, it has only a limited effect of 3-4 months for lactose-hydrolysed milk (LHM) [1]. This is especially due to the reactivity of the monomeric sugar leading to undesired browning and off-flavour development [2] which limits its exportation to distance markets. Formation of undesired volatile organic compounds (VOCs), mainly due to lipid oxidation and Maillard reaction, appeared to be a quality defect during prolonged LHM storage [2-3]. These undesired VOCs can impact the milk flavour, which might lead to consumer rejection of the LHM [4]. Hence, it is pertinent to further explore methods for extending LHM shelf life to enable global distribution and mitigate food waste.

This study aimed to investigate colour and VOCs development in pre- and post-hydrolysed UHT milk with different lactase preparations and stored for up to one year at 25 and 35 °C. For pre-hydrolysed milk samples, lactases were added to the milk before UHT treatment, and for post-hydrolysed milk, the lactases were added after UHT treatment. Samples were drawn at day 0, 14, 42, 70, 105, 140, 182, 224, 273, 315 and 364. In terms of measurements colour, pH, gas chromatography-mass spectrometry (GC-MS) and proton transfer reaction-mass spectrometry (PTR-MS) analysis were performed. For PTR-MS, samples were analysed in triplicates after incubation for 20 min at 40 °C with a commercial PTR-QiTOF-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria) operating in V mode. Headspace measurements were done for 40 seconds with an acquisition rate of one spectrum per second, a flow rate of 35 sccm and an E/N value of 135 Townsend. The dataset obtained by PTR-MS data extraction, performed by PTR-MS Viewer (Ionicon Analytik GmbH, Innsbruck, Austria), consisted of 216 mass peaks. A mass peaks selection was applied to reduce features resulting in 78 mass peaks on which principal Component Analysis (PCA) and one-way ANOVA with Tukey's Honestly Significant Difference (Tukey's HSD) post hoc test were performed to study differences induced by lactase preparations during shelf life.

The analysis showed that most of the volatilome variations of the milk samples, were induced by storage time and temperature. In terms of treatments, post-hydrolysed milk contained higher levels of the mass peak *m/z* 63.028 which was tentatively identified as dimethyl sulfide (DMS). On the other hand, pre-hydrolysed and conventional UHT milk samples showed higher concentrations of different mass peaks including alkyl fragments (*m/z* 41.043 and 43.055) and *m/z 61.037* tentatively identified as acetic acid especially in later stages of the shelf life. Increased storage temperature led to a decrease in pH in association with the acid formation. The lactase preparation also had an effect on the VOCs profiles with significant changes in concentrations reported for 19 different mass peaks. Post-hydrolysed milk stored at 35 °C for one year exhibited the greatest effect of lactase enzyme used. Especially Strecker aldehydes were influenced by the lactase preparation used in post-hydrolysis. The study also provided the first evidence that increased storage temperature affects the reaction kinetics of some VOCs related to Maillard reactions in post-hydrolysed milk as well as of some lipid oxidation VOCs such as methyl ketones and hexanal.

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Fast-GC PTR-MS Analysis of Coffee VOCs

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Abstract

A fast-GC PTR-ToF-MS method coupled to an autosampler, for analysis of volatiles above ground coffee samples has been developed and validated. The results have shown that many of the molecular formulas detected by PTR-ToF-MS, commonly associated with coffee volatiles, are composed of numerous overlapping compounds, as demonstrated by fast-GC separation prior to PTR-ToF-MS analysis.

Introduction

PTR-MS is the method of choice for on-line VOC (volatile organic compound) analysis of dynamic food processes. The high sensitivity and good temporal resolution makes PTR-MS highly suitable for such applications. In particular, the technology has found numerous uses in the coffee aroma research [1-3]. The high sensitivity of PTR-MS has also made it suitable for rapid analysis of coffee samples, when coupled to an autosampler[1]. By use of ToF (time-of-flight) mass detector, the tentative identification based on molecular formulas of analytes and known composition of coffee VOCs is possible. However, tentative identification can result in ambiguous data.

The aim of this work was to explore the possibility of using a fast-GC for a rapid separation of coffee VOCs before detection with PTR-MS. This provides considerably better resolved compounds and much improved identification and qualification. The drawback of the methodology is the complexity of the experimental setup and data analysis and the reduced sample throughput, compared to direct injection PTR-ToF-Ms without coupling to fast-GC

Experimental Methods

A washed Colombian arabica Coffee was roasted to a light roast level (125 Colorette Pt, measured by Colorette 4, Probat AG, Germany) using a 1 kg batch size Probatino roaster (Probat AG, Germany). Coffee was ground to a filter coffee grind size (800 um average particle size) and packaged in coffee bags until analysis.

An MPS autosampler (Gerstel GmbH, Germany) was used, equipped with a PurgeXL unit for dynamic headspace analysis. For the analysis 2 g of ground coffee was transferred into 20 mL glass vials. The autosampler sequence involved the following tasks: preheat (incubate) the vials in an agitator unit to 85 °C for 5 min, then transfer the vials into the PurgeXL unit at 80 °C for dynamic headspace sampling. The sampling started only after the vial was 1 min on the PurgeXL unit. Further details of the PTR-MS – Autosampler interface are described in literature[1,3].

The headspace of the vials was flushed for 1 min, with 10 nmL/min of nitrogen. An additional 50 nmL/min of nitrogen was added to the flow to generate enough flow for a reproducible transfer of the sample to the fast-GC. A 100 µL loop was being flushed with the gas from the autosampler and the fast-GC program was started at 5 s after vial flush for static headspace measurement or after 1 min after start of vial flush for dynamic headspace measurement.

The fast-GC time temperature profile was as following: 10 s at 40 °C, then 10 °C/s until 200 °C. The outlet of the fast-GC was connected to the PTR-ToF-MS 6000x2 (Ionicon GmbH, Austria). The fast-GC unit is integrated into the PTR-MS and contains a 10 m, 0.25 mm i.d. metal capillary, coated with non-polar MXT-1 sorbent. The PTR-MS was operated at 140 E/N.

Results and Discussion

The validation of the method included optimization of the sampling setup parameters, which have been found critical for reproducible analysis. In comparison with the traditional GC/MS the fast-GC PTR-MS unit does not have an inlet liner as a traditional GC but injects a sample to the column via a loop by a two-position multi-position valve. Because the amount of sample in a 20 mL vial is small, the timing for the injection is critical for optimal sensitivity and reproducibility. An adjustable delay unit has been developed for this purpose to inject the sample into the fast-GC at the point of highest concentration. The optimal conditions for our system were found to be 5 s after the start of dynamic headspace flushing of the vial.

The temperature gradient GC run time was limited by cooling of the fast-GC unit and the need to incubate the vials to 80 °C before headspace sampling. Total throughput of the samples was 4 min. Lower incubation temperatures could allow slightly higher throughput; however, the sensitivity of the method would decrease.

PTR-MS analysis collects a large amount of data in a short time, and the additional chromatographic separation dimension creates a challenge in data analysis. Hence, a major part of this study was to create a data analysis tool using R statistical computing, to sort and consolidate the data processed by Ionicon IDA software (Ionicon Data Analyser), and finally to integrate the chromatograms by each m/z detected by IDA software. This was achieved by peak fitting chromatograms using Gaussian function.

In total 174 m/z peaks were detected by the IDA software from the fast-GC PTR-MS analysis of headspace above roast and ground coffee. This is only slightly less than direct injection PTR-MS of coffee samples.[1] We have found clear examples where previously tentatively identified m/z as measured by PTR-ToF-MS do not correspond to only one compound, but to more than one compound. Such example is presented in Figure 1 for tentative identification of 2,3-butanedione, where fast-GC analysis reveals an additional compound at m/z 87.04167. Examples of similar situations where more compounds are resolved by the fast-GC, have been found for the following compounds (tentatively identified): 2-methyl pyrazine, 2,3-pentadione, 5-methyl furfural.

Fast-GC is a powerful method to increase the identification power of compounds detected by PTR-MS. For static experiments coupled to autosampler or sampling of packaging headspace it is a powerful and rapid method. However, the complexity of data and the lack of availability of integrated data analysis tool makes fast-GC data analysis highly time consuming and is rather suitable for targeted PTR-MS analysis than fingerprint analysis. In addition, the thermal stability of the fast-GC seems more critical than traditional GC as the retention times were less reproducible than expected.

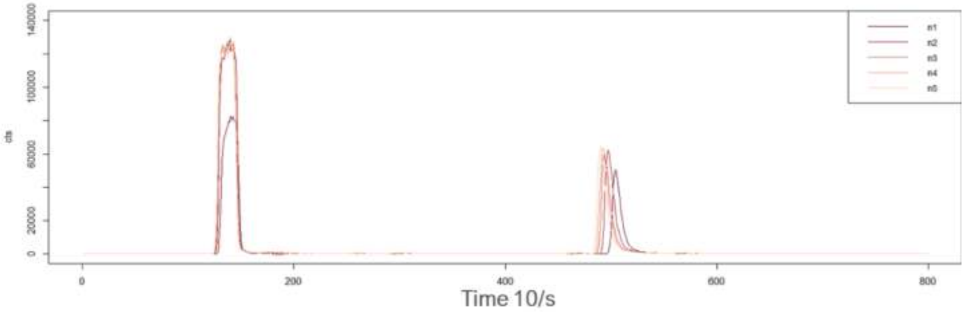

Figure 1: Fast-GC PTR-MS chromatogram of the m/z 87.04167 sampled from the headspace of a roasted and ground coffee sample. The m/z 87.044 is typically tentatively assigned as 2,3-butandione (the fast-eluting peak). However, a second much less volatile compound with the same molecular formula is present in a considerable amount (second peak), here tentatively identified as γ-Butyrolactone. Lines n1-n5 are 5 consecutive Fast-GC PTR-MS replicates.

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Comparative Analysis of Volatile Abatement Systems from Cooking Emissions

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Abstract

Volatile organic compounds (VOCs) are molecules present in our everyday life, and they can be positive, such as in the formation of odour and food flavour, or harmful to the environment and humans, and research is focusing on limiting their emissions. Various methods have been used to achieve this purpose. Firstly, we review three main degradation methods: activated carbon, photocatalysis and a synergetic system. We provide a general overview of the operative conditions and report the possibility of VOC abatement during cooking. Within the literature, none of these systems has ever been tested in the presence of complex matrices, such as during cooking processes. The aim of this study is to compare the three methods in order to understand the behaviour of filter systems in the case of realistically complex gas mixtures. Proton transfer reaction–mass spectrometry (PTR-MS) has been used in the real-time monitoring of volatilome. Due to the fact that VOC emissions are highly dependent on the composition of the food cooked, we evaluated the degradation capacity of the three systems for different burger types. We demonstrate the pros and cons of photocatalysis and adsorption and how a combined approach can mitigate the drawbacks of photocatalysis.

Introduction

During cooking, many volatile organic compounds (VOCs), chemicals that easily evaporate at room temperature, are continuously produced and released into the air. Some of these molecules are fundamental in food characterization because they contribute to both flavour and odour formation [1]. On the one hand, VOCs play a vital role in the aroma and taste perception of food products, contributing to their overall sensory quality; however, on the other hand, some of these compounds are known human carcinogens, and other suspected carcinogens are also under study. The production of VOCs in food is a complex process influenced by various factors, such as food composition, processing conditions, and microbial activity. The primary process regarding food cooking is the Maillard reaction: a complex chemical reaction that occurs between amino acids and reducing sugars, usually at elevated temperatures. Strecker degradation is relevant in the subset of final Maillard reactions [2]. The last major VOC production mechanism during cooking is lipid oxidation. Thus, it is already known that cooking processes produce several types of VOCs, among which several can be of concern in terms of the environment and long-term health, such as formaldehyde, methanol, acetaldehyde, acetone, and acetic acid [1,3]. Two typical methods of VOC degradation for indoor applications are activated carbons (AC) and photocatalysis (PC). However, these two methods have some drawbacks, such as high energy consumption and environmental incompatibility [4].

A possible way to avoid both drawbacks of the aforementioned methods is to combine adsorption and photocatalysis in carbon-based nanocomposites, such as activated carbon (AC) coupled with nano-TiO_2.. A possible advantage of carbon-based nanocomposite paired with photocatalysis is the prevention of the generation of intermediates, which are immediately captured by charcoal, and the inactivation of the catalyst [4].

An interesting challenge, which, to the best of our knowledge, has not been addressed within the literature, is the evaluation of the behaviour of AC/PC technology related to a complex mixture of VOCs, focusing on the emissions generated during cooking. In such a scenario, it would be worth investigating the compensation of the defects present in each method when used alone and if VOCs with low adsorption rate in AC are oxidized by PC. Furthermore, it would be important to evaluate the intermediate compounds and their possible interference with air cleaning processes. This work aims to compare the performance between adsorption, photocatalysis, and combined systems in abating the complex VOC matrices produced when cooking three different types of hamburgers: meat, greens, and fish. The objective of this research is to determine whether the synergy between adsorption and photocatalysis is useful in the removal of VOCs from indoor air for residential usage. The air purification system that was employed for this project was created in view of possible applications in fume hoods in the future. PTR-MS was employed to monitor VOCs in real-time, thus providing time-resolved data on VOC emissions and abatement. Several studies [1,5,6] have already demonstrated the possibility of PTR-MS on VOC monitoring and quantification, and in this work, we also aim to show the potential of this technique to evaluate the performance of air cleaning systems in abatement of VOC mixtures.

Experimental Methods

All filters used as air purifier were manufactured by Elica S.p.A (Fabriano, Italy). The photocatalytic system is composed of 2 tiles of titan dioxide with 4 LED UVA each (peak at 367 nm) and powered using 3.6 V. It has a TiO_2 loading weight of 2.5 ± 0.5 g, an LED power of 20.8 W, and an average irradiance of 28 mW cm^{-2}. The adsorption material is a ceramic-reinforced activated carbon composite; a single filter is composed of 4 honeycombs with a cell density of 676. Measurements were performed in an 8 m^3 polyethylene (PE) chamber, and, before the cooking experiments, ambient sampling was conditioned with purified air. The pollutant abatement systems were installed in the middle of the chamber beside a hotplate. In each measurement, after conditioning the chamber, a burger was placed in a pan and cooked on a hot plate with a set power of 1000 W for 5 min. The plate was then switched off, the air in the chamber was given 15 min to homogenise, and then the purification system was turned on for 90 min. This value of the sampling time was chosen because it is comparable with the median working time of an extractor hood for home use during cooking. The instrument used for VOC measurement is a PTR-MS equipped with a quadrupole detector. The sampling flow was set to 40 sccm, while the method used to collect data involves a full scan from 20 *m*/*z* to 250 *m*/*z*.

Results and Discussion

To offer a comprehensive view of the global dataset, we conducted separate PCAs for each type of burger, representing all three abatement systems together on a single plot (Figure 1). The scores show interesting trends: upon cooking, the VOCs in the chamber change dramatically; however, when the purifying system is turned on, the VOC composition in the chamber either almost returns to the starting point (in the case of "Activated Carbon" and "Combined") or moves away (in the case of "Photocatalysis"). It is worth noticing that in no case did the original VOC configuration seem completely re-established after 90 min of purifying system operation. Regardless, the synergetic setup seems to be able to compensate for the negative aspects of photocatalysis. In fact, the results of "Activated Carbon" and "Combined" are rather similar.

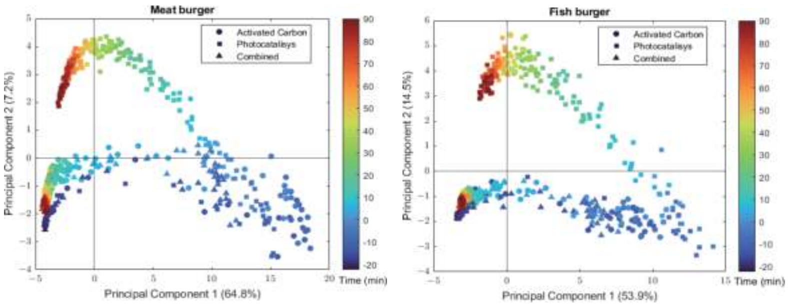

Figure 1: PCA plot PC2 vs. PC1. The three abatement systems are reported in the same plot. The blue colour refers to the start of measurement, while the red colour refers to the end.

The trend of the five compounds that showed the highest concentration was specifically reported. The selected compounds were acetic acid (m/z = 61), acetaldehyde (m/z = 45), formaldehyde (m/z = 31), methanol (m/z = 33), and acetone (m/z = 59). For space reasons, here we present only the case of acetaldehyde in fish burgers.

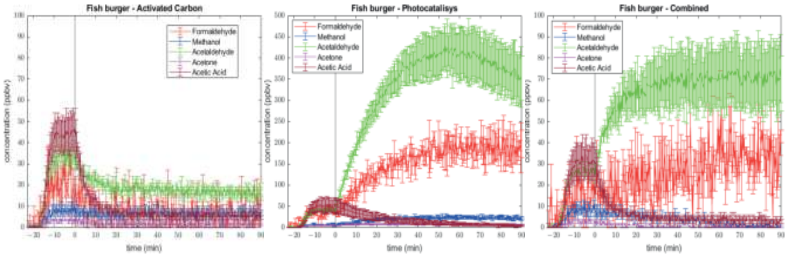

Figure 2:Cconcentration vs time plot of five selected VOCs. There are reported fish burgers and for each, the three purifying methods. Data are means ± standard error.

Acetaldehyde is produced upon cooking meat burgers (ca. 80 ppbv), vegetable burgers (50 ppbv), and fish burgers (30 ppbv). The first anomaly that can be noticed compared to the other volatiles is in the photocatalysis technique applied to the fish burger: after the conditioning of the sampling space with the cooked burger volatilome and the ignition of TiO_2 LED, a significant production of acetaldehyde occurred, with a peak of almost 450 ppbv. These are the highest concentration values high amount of acetaldehyde as a by-product, which pollutes the chamber. In the activated carbon filter applied to the cooking emissions of the fish burger, the acetaldehyde amount is small and constant during time, likely due to the saturation of coal porosity. As it emerges from the combination with photocatalysis, the introduction of carbon as an adsorbent material enables limiting the negative effects of photodegradation, keeping its value stable over time. In the experiments using the meat burger, upon the activation of the air cleaning system, acetaldehyde follows the trend of those measured for the fish burger, but with smaller concentration values, which is why adsorption with coal in combined system mitigates the influence of photocatalysis. In the case of the vegetable burger, no increase in acetaldehyde is detected when using the “Combined” system, while, as expected, there is a small increase when using the “Photocatalysis” system.

Conclusions

We manage to apply PTR-MS for real time assessing of the efficiency of major indoor air treatment methods. The sample used are representative of three major categories of foods and technique performance is highly dependent on burger composition. Acetaldehyde seems to have low compatibility with “Photocatalysis” because the technique increases the concentration producing intermediates of oxidation of complex VOCs. Anyway, the presence of coal and integration of adsorption mechanism manages to limit acetaldehyde growth. Thus, synergetic coupling seems to be a promising technology for abatement of cooking emission.

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Applications in Health Science

The role of PTR-MS in quality assurance in breath analysis

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Abstract

Proton transfer reaction-mass spectrometry (PTR-MS) has become an important analytical technology in the field of breath research, foremost due to its ability to analyze volatile organic compounds (VOCs) in exhaled breath directly and in real-time. The technique is well suited to targeted analysis of individual compounds, often accompanied by complementary validation using gas chromatography-mass spectrometry (GC-MS) for confirming compound identities. Within the field of breath analysis, but beyond the analysis of breath itself, PTR-MS represents a useful tool in quality assurance assessments. This talk will review recent endeavors in breath sampling and standardization, including terpene washout benchmarking tests, adsorption and emissions of volatiles from sampling materials, and material emissions assessments in view of inhalation exposure limits.

Introduction

The concept of breath analysis for health applications has existed for many decades, yet recent years have seen increased interest and activities in this field [1]. Several breath tests have been established and are in clinical or non-clinical use, such as capnography to monitor respiration, exhaled nitric oxide for asthma therapy monitoring, the breathalyzer to test for sobriety via exhaled ethanol, as well as some targeted metabolism tests using labeled substrates [2]. Despite the value and relative successes of this handful of applications, the scope of breath tests for further and routine uses is narrow. Developing breath tests is a challenging undertaking due to the complexity and diversity in terms of target compounds and diseases, as well as the persistent presence of confounding variables and analytical variations. These limitations are well known in the breath research community [3]; consequently, several initiatives have been proposed and conducted to test and ensure analytical fidelity and reduce the risk of confounders disrupting breath datasets.

Discussion

PTR-MS exhibits unique analytical capabilities for its implementation in quality assurance assessment in the field of breath research. Example applications for which PTR-MS technology has been utilized to gain an understanding of different aspects of breath sampling and analysis are outlined in the following.

Benchmarking

A recent standardization endeavor, termed the *Peppermint Experiment*, aimed to develop and establish a breath testing protocol as a benchmarking test for cross-validation of sampling and analysis approaches for breath [4]. The protocol involves the ingestion of a peppermint oil capsule for subsequent monitoring of its volatile terpene constituents in breath during their washout from the body. Several institutions contributed to the *Peppermint Experiment* and published combined data on breath washout profiles using common techniques, e.g., either direct injection mass spectrometry (PTR-MS or selected ion flow tube-mass spectrometry; SIFT-MS), gas chromatography-mass spectrometry (GC-MS), GC-ion mobility spectrometry (GC-IMS), or secondary electrospray ionization-mass spectrometry (SESI-MS). Despite the reasonable degree of alignment in washout datasets between similar analytical techniques, no specific comparison was made between the techniques themselves.

To address this issue, a study was undertaken to compare washout profiles determined by the analysis of common breath samples from the same volunteers using different analytical platforms. Specifically, PTR-MS, GC-IMS and GC-MS were employed for consecutive sampling and analysis of breath samples from 21 participants for cross-validation of the different approaches following the workflow depicted in figure 1. Common mean washout times of 448, 448 and 372 min were observed for PTR-MS, GC-IMS and GC-MS, respectively, indicating excellent reproducibility across these techniques [5].

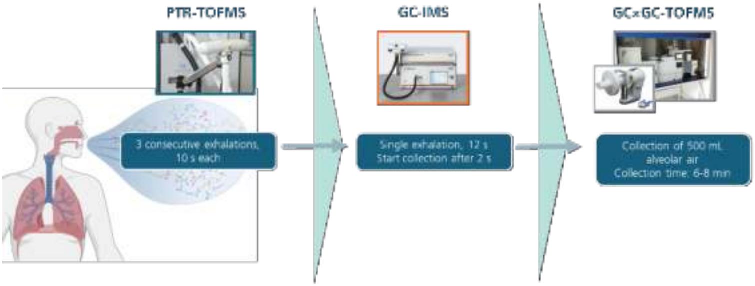

Figure 1: Breath collection and analytical workflow for the analytical platform cross-validation benchmarking study using the Peppermint Experiment protocol.

Adsorption and Emissions

The ubiquity of volatiles in the (indoor) environment is a well-known critical source of confounders in breath analysis, with much debate as to how these should be accounted or corrected for [6]. One source of volatiles that has been less well explored, however, is the breath sampling device, whose materials present a local and immediate potential to confound breath samples. On the one hand, emissions from the mouthpiece materials can disrupt the composition of the breath matrix by the addition of specific compounds or by masking others already present in breath. On the other hand, breath constituents at trace concentrations might be lost to the sampling system through adsorption to the inner surfaces of the mouthpiece. In a recent study, PTR-MS was used to examine the degree of emissions or uptake of breath-relevant volatiles from or to different sampling systems [7], with a related schematic depicted in figure 2.

Using the liquid calibration unit (LCU) to supply either clean humid air or generate a gas mixture containing breath-relevant volatiles at different concentrations, various mouthpieces were placed in-line between the LCU and a PTR-TOFMS for direct analysis of volatiles emerging at the downstream end of the mouthpiece. The results indicated varying degrees of uptakes and emissions, depending on the compounds and materials, as reported in a recent publication [7]. Specifically, ketones and aldehydes, as well as sulfur and nitrogen-containing compounds had relatively low uptake in the materials that were tested, albeit with high emissions of the ketones in a silicon mask that is commonly used in breath sampling. In contrast, carboxylic acids where adsorbed by most materials to a relatively high degree, indicating the danger in losing such compounds during sampling. Overall, the outcomes of that study demonstrate the utility of PTR-MS for assessing confounders in breath research and shed light on the suitability of different materials for their use in breath sampling mouthpiece interfaces.

Figure 2: Schematic depicting the purging of a breath sampling mouthpiece with breath-relevant volatiles or clean, humid air to assess the degree of compound uptake of the former or emissions into the latter, as is of relevance for potential confounding effects for breath samples.

In another recent study, PTR-MS was coupled to a micro-chamber/thermal extractor (µCTE) as a means to assess volatile emissions from different materials, specifically resins used in 3D printing [8]. This novel approach allowed the compound-dependent emissions to be traced in real-time under different temperature conditions. Furthermore, material treatment protocols, e.g., autoclaving, were assessed for their efficacy in reducing emissions, with the analyses demonstrating a marked reduction in all compounds across the three resin materials that were tested. Finally, using the ensuing data, the emission rates could be calculated, with a subsequent determination of acute exposures during breath sampling, as experienced when inhaling through the polymer materials of breath sampling mouthpieces [9].

Conclusion

PTR-MS represents a versatile tool in the field of breath that is not limited to the analysis of exhaled breath itself, but through its use in other quality assurance assessments, such material emissions and uptakes, as outlined here. The methods developed for such evaluations, especially the use of the LCU to challenge materials with breath-relevant gas mixtures, or the coupling of PTR-MS to the µCTE device for targeted emissions analyses under defined conditions, represent novel approaches towards improving breath analysis and minimizing the inhalation of harmful substances. Using these methods, further work can be undertaken to explore the emissions for exposure assessments of a wider variety of polymer materials, including rapid assessments as an initial screening to determine the suitable of novel materials for use in breath sampling mouthpieces.

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Enhanced proton transfer reaction - mass spectrometry breath analysis for the diagnosis of COVID-19

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Introduction

While there is an urgent need for rapid screening and diagnosis of COVID-19, conventional testing methods are time-consuming and expensive. Proton transfer reaction - mass spectrometry (PTR-MS) breath analysis, a non-invasive point-of-care technique based on detecting volatile organic compounds, may be a promising tool for addressing this challenge.

Aim

The aim of this study was to assess whether artificial intelligence-enhanced PRT-MS breath analysis could be a reliable, safe, rapid means of screening ambulatory patients for COVID-19.

Methods

In two prospective, open, interventional studies in a single university hospital, we used PTR-MS to perform a metabolomic analysis of exhaled breath from adults requiring screening for COVID-19. Artificial intelligence and machine learning techniques were employed to construct mathematical models using breath analysis data alone or in combination with patient metadata.

Results

Breath samples were collected from 173 participants, including 67 with confirmed COVID-19. After processing breath analysis data and refining the machine learning model by incorporating patient metadata, the method successfully differentiated between COVID-19-positive and -negative participants (sensitivity: 98%, specificity: 74%, negative predictive value: 98%, positive predictive value: 72%, area under the ROC curve: 0.961). The predictive performance remained consistent across asymptomatic, weakly symptomatic, and symptomatic participants, and it was not influenced by COVID-19 vaccination status.

Conclusions

Real-time, non-invasive, artificial-intelligence-enhanced PTR-MS breath analysis emerges as a potentially reliable, safe, rapid, cost-effective, and high-throughput method for COVID-19 screening.

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Clinical Applications of Exhaled Volatiles

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Abstract

Here we will discuss the advantages and disadvantages of Proton Transfer Reaction/Selective Reagent Ion-Mass Spectrometry (PTR/SRI-MS) to analyze breath volatiles for applications in the health sciences, with a focus on the potential development of diagnostically useful clinical breath test devices. After decades of research, no soft chemical ionization mass spectrometric investigation has identified any endogenous volatile organic compounds that provide biomarkers or fingerprints to diagnose a disease [1, 2]. The reasons for this are manifold, and these will be briefly discussed and examined. Originally considered a nuisance by many in the field of breath research, it is now becoming realized that exogenous, rather than endogenous, breath volatiles have a greater potential of being exploited as useful metabolic probes to the human body, capable of providing unique biomarkers for use in diagnostically useful tests that could be clinically acceptable. An example of this comes from a PTR-MS study of liver disease, for which we found statistically significant higher levels of the exogenous compound limonene in the exhaled breath of volunteer patients suffering from cirrhosis compared to the levels observed in the exhaled breath of healthy controls [3]. More importantly, for those patients who went on to have a liver transplant, it was found that following surgery their exhaled levels of limonene continuously dropped and returned to normal values within several days. This provided the first positive proof that increased levels of limonene in the exhaled breath of cirrhotic patients are directly related to liver disease. To take this biomarker discovery further requires a limonene breath test using an analytical device that is more portable, more user-friendly and cheaper than PTR/SRI-MS. Sensor-based systems would be ideal for this, providing that high chemical selectivity for a diagnostically useful volatile, such as limonene, can be achieved. For such developments, PTR/SRI-MS can play a significant role by utilising its real-time analytical capabilities to test, characterize and validate prototype sensor devices. However, given the high humidity contained in exhaled breath samples, a potential obstacle to this PTR/SRI-MS application will occur if the product ions of a volatile of clinical interest react with the water vapour present in the drift tube and lead to non-specific secondary product ions. Such secondary ion-molecule reactions will then result in a reduction of the instrument's analytical sensitivity to the detection of that particular volatile. This limitation has been observed for sevoflurane, an inhalation anaesthetic, and its metabolite, hexafluoroisopropanol, both of which have been proposed as potential volatile probes to non-invasively assess liver function [4]. To overcome the humidity dependent analytical sensitivity for the detection of these two volatiles, a Nafion^{TM} membrane filter was inserted into the inlet line of a PTR/SRI-MS to deliver exhaled breath samples with reduced humidities [5]. We suggest that this technique could be usefully adopted to other areas of PTR/SRI-MS research when the humidity of a gas sample reduces the sensitivity of the instrument to the volatiles of interest.

Introduction

Nearly 1500 trace volatile organic compounds have been found in exhaled breath [6], with detected volume mixing ratios ranging from sub-parts per trillion by volume up to hundreds of parts per million by volume. These volatiles can have endogenous (systemic) origins, which result from normal and abnormal metabolic activities or pathological disorders, or are exogenous in nature, resulting from the ingestion, inhalation or dermal absorption of chemicals and substances, or they can have contributions from both endogenous and exogenous sources. There are a number of limitations of employing PTR/SRI-MS for volatile breath analysis, which will limit its analytical use to diagnose disease or to monitor therapeutic treatments in a clinical setting. Nevertheless, it will be shown that PTR/SRI-MS can be an extremely useful analytical monitoring device for on-line quantitative analysis without the need for sample workup. It will also be demonstrated how PTR/SRI-MS can be used as a valuable analytical tool for continuous on-line real-time health related studies. This real-time advantage of the PTR/SRI-MS technique can be applied to provide breath resolved analytics, allowing the end-tidal phase of an exhaled breath to be easily identified, and for use in characterizing portable and clinically user-friendly novel sensor-based breath test instruments for use in disease diagnosis, including the diagnosis of bacterial and viral infections.

Discussion

Endogenous Breath Volatiles and Human Metabolic Processes

Since the earliest applications of the very first prototype [7-10], PTR-MS has been extensively used to detect and investigate the trace volatile organic compounds that are found in exhaled breath, with a particular focus on potential applications in the health sciences [1, 11, 12]. Many of these studies are associated with clinical attempts to find exhaled volatiles that are associated with a disease, with the assumed expectation that volatiles found in the advanced stages of a disease are present in the early stages. At first glance this appears to be a sensible approach, given that exhaled volatiles, and especially those that are endogenously produced, reflect changes in metabolic processes occurring in the human body. However, this holy-grail for breath research has remained elusive. Not one PTR/SRI-MS investigation, or for that matter any other mass spectrometric study, has been able to link endogenous volatiles to a disease with any level of confidence. The reasons for this include poor sampling, a lack of standardization, poor experimental methods, poorly designed clinical trials, ignoring ventilation and perfusion, disregarding the influences of diet, environmental exposure and medication, a lack of knowledge on the biological origins of the breath volatiles, and poor statistical analysis (leading to voodoo correlations). However, even if such factors are taken into account, it is still unlikely that endogenous volatiles will be able to provide unique signatures to identify a diseased state [2]. This is because they are simply not specific enough, i.e., volatile metabolites can often be attributed to several metabolic processes. Nevertheless, a potential use of exhaled endogenous volatiles comes from a person acting as their own self-control, for which it has been proposed that after establishing a normal volatilome profile, a yearly personalized breath test could provide comparative measures of changes in oxidative stress/inflammation volatile biomarkers [2]. An elevation in such biomarkers, compared to previous breath tests, could indicate that a health issue is developing that requires further investigative diagnostics to identify a possible disease. There are other significant advantages in applying PTR/SRI-MS for endogenous volatile analysis, including its ability to undertake real-time and almost continuous measurements. This is highlighted in an early on-line trace gas PTR-MS study by Jordan *et al*, who were the first to observe the sudden increase in exhaled isoprene within ~ 1 minute following commencement of exercise, which is then followed by a fast drop over several minutes [13]. This behaviour was later investigated in detail by King *et al* and successfully modeled using the hypothesis that isoprene is mainly produced in muscle tissue and not in the liver [14]. Such studies have inspired considerable debate on the origins and role of isoprene in the human body. Although the purpose of isoprene production in muscles still remains uncertain, an important multi-omic investigation of genes and metabolites by Sukul *et al* has recently confirmed that isoprene results from muscular lipolytic cholesterol metabolism [15].

Exogenous Breath Volatiles and Human Metabolic Processes

There has been a growing realization that exogenous compounds, and any resulting volatile metabolites, provide ideal probes to metabolic processes that have significant potential for use in personalized medicine, e.g., to monitor disease progression or for determining the efficacy of drugs and other therapy treatments. Towards this goal, we have been undertaking both *in vitro* and *in vivo* investigations to provide underpinning knowledge that can help to enhance the development of non-invasive exogenous metabolic volatile breath tests. Here we highlight some of our PTR/SRI-MS *in vivo* research, focusing on (i) breath volatiles and liver disease [3] and (ii) pharmacokinetic studies of sevoflurane, a commonly used inhalation anaesthetic, and its metabolite, hexafluoroisopropanol (HFIP) [5, 16], which mainly deal with the washout of these volatiles from the body following an operational procedure or from occupational exposure; this has formed part of a major clinical study to determine the factors that influence the lifetime of inhalation anaesthetics in the human body.

(i) Limonene and Liver Disease: meeting an unmet medical need

The last 30 years has seen an approximate 30% rise in deaths worldwide associated with liver cirrhosis. A major problem is that liver disease progression is asymptomatic, making diagnosis challenging. Often patients do not present symptoms until the disease is fairly advanced, leading to more than 50% of people affected by liver disease receiving their first diagnosis at a late stage [17]. Even then, late-stage liver disease diagnosis is difficult because symptoms are often general and can be mistaken for other causes. An aim of our work is to address an unmet medical need for non-invasive procedures that can routinely and regularly test and screen for liver disease, determine liver function, and evaluate the efficacy of treatments or changes in lifestyles. The PTR-MS study that linked elevated breath limonene levels to liver disease crucially used patients as their own self-controls in a targeted phase approach [3]. This permitted comparisons of patients' breath profiles pre- and post-liver transplant, thereby ruling out putative biomarkers resulting from false discovery. To take this work forwards, i.e., towards a breath test, a prototype near-to-real time dynamic and selective sensor for limonene has been developed, with the sensor's chemical selectivity capabilities having been confirmed by the use of simultaneous PTR-MS cross-validation measurements [18].

(ii) Monitoring Sevoflurane and its Metabolite Hexafluoroisopropanol

Determining the washout times of sevoflurane and its metabolite, HFIP, from the human body are important for the post-operative recovery of patients as well as for determining the workplace exposure of hospital staff [5, 16]. However, the sensitivity for the detection of these volatiles is found to be dependent on the buffer gas humidity in the drift tube (reaction region) of the PTR/SRI-MS. To overcome this problem, a Nafion^{TM} membrane filter was inserted into the heated inlet line of a PTR/SRI-MS in order to reduce the humidity of breath samples prior to their introduction into the drift tube [5]. The success of this approach was initially confirmed through a comparison of the product ion intensities measured in dry (relative humidity (rH) $\approx$ 0%) and humid (rH $\approx$ 100%) nitrogen gas containing traces of the volatiles, with and without the use of the membrane filter, and then practically from the analysis of postoperative exhaled breath samples from volunteer patients.

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Studies of Volatile Compounds Produced by Pathogenic Oral Bacteria

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Abstract

We have studied the volatile metabolites produced *in vitro* by pathogenic oral bacteria and the potential of these volatiles as future biomarkers for oral infections. We sought to examine whether oral pathogens associated with oral infections can be distinguished based on the volatile organic compounds (VOCs) they produce and what is the connection of the VOCs to the bacterial metabolism. The overarching goal has been to investigate the possibility of developing a breath test for oral infections. For this reason, we have also investigated the presence of these microbial VOCs in the exhaled breath of volunteers. Measurements were performed using a combination of proton-transfer-reaction mass spectrometry (PTR-MS) and gas chromatography–mass spectrometry (GC-MS)

Introduction

Bacterial induced oral diseases are a global problem [1]. Inflammation of the gum tissue, known as gingivitis, is the second most common oral disease (after caries), affecting over 75% of people. Untreated, gingivitis may develop into a more severe inflammatory disease, known as periodontitis, which leads to destruction of the tooth-supporting tissues. Over 11% of the whole adult population have severe periodontitis and 9–30% of elderly people worldwide have no natural teeth. Most oral infectious diseases can be prevented by maintaining good oral hygiene and regular visits to a dental practitioner. Early diagnosis and subsequent treatment promote positive outcomes and reduce associated costs. Novel methods for rapid identification of the cause of the infection, in other words the identification of the bacteria involved, could aid in early diagnosis. Measuring volatile metabolites of pathogenic oral bacteria from the exhaled breath of a patient could provide a non-invasive and easy method to assist in the clinical assessment of oral infections.

Experimental Methods

We have used the combination of PTR-MS (Ionicon PTR-TOF 1000) and GC-MS to measure and identify the VOCs emitted by oral bacteria *in vitro*. Online measurements over the different phases of bacterial growth were performed using PTR-MS [2,3,4]. Structural identification of the bacterial volatiles was confirmed by a combination of solid phase microextraction (SPME) and offline GC–MS [3,4]. Same analysis techniques were used for the exhaled breath measurements of volunteers [5].

The *in vitro* measurements concentrated on four pathogenic oral bacteria connected to periodontal disease and dental abscess: *Porphyromonas gingivalis* (three separate strains), *Prevotella intermedia*, *Prevotella nigrescens* and *Tannerella forsythia*. Volatile fingerprints were measured from the headspace gas of the bacteria cultured on agar and in liquid nutrient broth. We also studied whether metabolic changes and bacterial viability can be evaluated via bacterial volatiles. This was performed by analyzing the effects of antibiotic treatment and limited supplemental iron availability on the VOC profiles of the bacteria

In the *in vivo* part of the work, we analyzed the exhaled breath of healthy volunteers in the morning straight after waking up, and after tooth brushing. The aim was to determine compounds, whose amount significantly decreased after tooth brushing compared to the morning breath. These compounds were assumed to be most strongly linked to the oral cavity, and moreover, to the oral bacteria.

Results and discussion

We have established that pathogenic oral species *P. gingivalis*, *P. intermedia*, *P. nigrescens,* and *T. forsythia*, all strongly connected to the development of periodontitis, produce distinctive combinations of VOCs [2,3]. For example, specific markers for *P. gingivalis* include 2-methyl-1-propanethiol, 6-methyl-1,2,3,4-tetrahydroquinoline, and isoamyl ester. These combinations of VOCs can potentially be used to distinguish oral pathogens from one another. Moreover, the studied bacteria produce several common compounds, such as indole, methanethiol, and short-chain fatty acids, which could be used to estimate the overall growth of these periodontal pathogens.

Methanethiol and hydrogen sulfide are strongly linked to the active growth of the bacteria, while short-chain and medium-chain fatty acids were produced mostly in the stationary-phase and the death-phase of the bacterial life cycle. Indole was produced throughout the growth, which suggests a connection to the undisturbed metabolic functions, as well as to the stress-response of the bacteria. Indole production was also found to increase, when *P. gingivalis* was under antibiotic threat, which further indicates a connection to stress-response. Limiting the supplemental iron-source available to *P. gingivalis* led to the decrease in the production of all other observed VOCs, except acetic acid [4].

Most of the VOCs identified as tentative biomarkers for *P. gingivalis*, *P. intermedia*, *P. nigrescens*, and *T. forsythia*, were also found from the exhaled breath of healthy volunteers in the morning breath measurements [5]. Tooth brushing cleared some of these from the breath, but others remained there in levels potentially exceeding the odor threshold even after oral cleaning. Consequently, the VOCs produced by the studied oral pathogens can also contribute to the breath malodor, even in healthy individuals. The levels are likely higher in people suffering from periodontitis, as there is a strong connection between bad breath and the periodontal disease. The results of our work prove that oral bacterial VOCs are found in the human exhaled breath. This provides a steppingstone for the future development of breath tests for periodontitis and other oral infections.

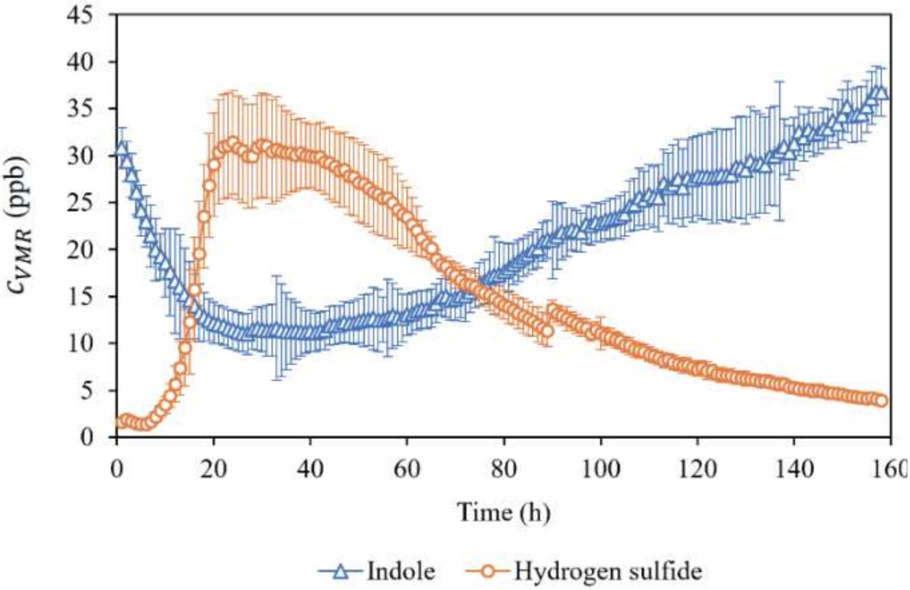

Figure 1: Production profiles of volatile indole and H_2S measured with PTR-MS from the headspace of P. gingivalis ATCC 33277 cultured on agar. Hourly volume mixing ratios are reported as the mean ± standard deviation (SD) of triplicate measurements. Indole production between 0 – 40 hours is due to emission from the Brucella agar.

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New data normalisation methods for PTR-TOF-MS exhaled breath metabolomics

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Abstract

Volatilomics is the branch of metabolomics dedicated to the analysis of volatile organic compounds (VOCs) present in exhaled breath for medical diagnosis and therapeutic monitoring. Data normalization is an important step to eliminate undesirable variations originating from non-biological factors. Issues such as batch effects and diminished sensitivity over time can be observed with PTR-MS, necessitating careful consideration to prevent bias when comparing samples collected over months.

We intended to evaluate established metabolomic data normalization methods and apply them to the analysis of exhaled breath PTR-TOF-MS data. We compared seven methods, five statistical-based methods and two using multiple standards metabolites, on two datasets from clinical studies on COVID-19 diagnosis [1, 2]. We assessed different means of feature selection to choose the standard metabolites, as well as the use of several repetition measurement of ambient air to train the normalisation methods.

We show that normalisation tools allow an increase in the diagnostic performance of the machine learning models, while decreasing the dependency with time. The sensitivity increased from 65% to 77% for the cohort from emergency room patients and the global accuracy was improved from 93% to 96% for the cohort from intensive care patients.

Our results highlight the importance of adding an appropriate normalization step during the processing of PTR-MS data, leading to substantial enhancements in the predictive capabilities of statistical models.

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Dynamic nature to metabolic pathway: PTR-MS based discovery of the human origin of breath isoprene

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Abstract

Isoprene is amongst the most abundant volatile metabolites produced by plants and animals. Human exhaled isoprene is extremely dynamic in nature and is related to various pathophysiology. Nevertheless, the endogenous origin was yet uncertain. Among 2000 individuals screened within consecutive mass-spectrometric studies, five healthy adults without breath isoprene were identified. Whole exome sequencing in these individuals revealed a shared homozygous (< 1% prevalent) *IDI2* stop-gain mutation preventing conversion of isopentenyl diphosphate to dimethylallyl diphosphate (DMAPP) in cholesterol metabolism. Targeted sequencing depicted that the *IDI2* variant is heterozygous in isoprene deficient blood-relatives and absent in unrelated isoprene normal adults. Wildtype *IDI1* and cholesterol metabolism related serological parameters were normal in everyone. *IDI2* determines isoprene production as DMAPP is the only source of isoprene and unlike plants, humans lack isoprene synthase and its homologue. Human *IDI2* is only expressed in skeletal-myocyte peroxisomes and instant spikes in isoprene exhalation during muscle activity confirm the origin from muscular lipolytic cholesterol metabolism. Well-defined endogenous origin translated isoprene as a clinically interpretable breath biomarker.

Introduction

Besides plants and animals, nearly all of us produce isoprene (1,3-pentadiene, C_5H_8) endogenously. It contains a C_5 hemiterpene unit essential for the biosynthesis of steroid hormones and terpenoids. It is the second most abundant volatile organic compound (VOC) in our breath and we continuously exhale it in trace amounts [1]. Thus, isoprene holds potential importance in clinical, pre-clinical, botanical and environmental sciences. <1% of our breath contains thousands of VOCs in trace concentrations. Since the dawn of modern breathomics, exhaled C_5H_8 has been described as a potential biomarker for diseases such as hypercholesterolemia, metabolic stress, muscle dystrophy, cardio-pulmonary diseases and various forms of cancers. Concentration changes are also related to various physiological and metabolic effects, inherited errors and to our biological ageing process [2]. Despite such attractiveness, until now this VOC could not be used in routine clinical practice as a biomarker. This was mainly due to its uncertain metabolic origin and biological functions involved in humans.

In 1984, Deneris et al hypothesized that cholesterol biosynthesis in the liver potentially gives rise to isoprene in our breath [3]. The belief was based on pre-clinical *in vitro* experiments. Nevertheless, changes and/or differences observed in breath isoprene under various conditions investigated in clinical studies could not be justified by the suggested origin. Though a few studies raised doubts about the hepatic source, concrete downstream proof was unavailable [4–6]. While absence of non-sterol isoprene is characterized as an indicator for inherited life-threatening conditions, since 1981, there were random reports of rare encounters of isoprene absent healthy adults. Isoprene absent healthy adults is rare (<0.3%) in the nature. Our previous investigations in such a healthy German adult and her family (isoprene deficient) disqualified its suggested origin from hepatic cholesterogenesis and depicted a recessive inheritance of this phenotype [7]. Nevertheless, a single case was insufficient for down-stream multi-omic investigations. Therefore, we started searching for rare adults in order to embark into down-stream investigations [8].

Experimental Methods

In consecutive clinical screening studies, we identified five healthy German adults without breath isoprene [8].

Therefore, to reveal the human origin, whole exome sequencing was conducted to identify unknown homozygous variants shared by these five (amongst 2000 recruitments) rare adults [8]. Shared mutations were checked via targeted sequencing in blood-related and unrelated (isoprene normal) adults. Plasma lipids, metabolites and hormones related to cholesterol metabolism were examined serologically. After having the ethical clearance, we reinvited the rare subjects. Signed informed consents were obtained prior to participation.

Down-stream investigations involved venous blood collection, peripheral blood mononuclear cells isolation, DNA isolation, multi-omics (breathomics, untargeted and targeted genomics) and serological metabolites analysis in healthy isoprene aberrated and isoprene normal adults[8].

PTR-ToF-MS methods for breathomics

All spontaneously breathing subjects maintained a defined posture and performed oral breathing 44 via customized mouthpiece or mask by following our state-of-the-are sampling protocol [7, 8]. Continuous side-stream sampling (flow: 20 – 100 mL/min) from the mouthpiece or mask were performed via the heated (75 – 100 °C) transfer-line of a PTR-ToF-MS-8000 or a PTR-ToF-MS-1000 (Ionicon Analytik GmbH, Innsbruck, Austria) under pre-optimized experimental conditions 70,71. Most importantly, PTR time-resolution of 200 ms, drift-tube temperature of 75 °C, voltage of 610 V and pressure of 2.3 mbar were used to reach the optimal E/N ratio of 139 Td. After automatic recording of a data file/min the mass scale was recalibrated based on masses namely, 21.0226 (H_3O^+-isotope), 29.998 (NO^+) and 59.049 (protonated C_3H_6O).

We used a PTR-MS viewer software (version 3.228) to process raw data. VOC data were measured continuously in counts per second (cps). Measured VOC counts were normalized to primary ion (H_3O^+) counts. Breath-resolved assignment of expiratory (alveolar/end-tidal) and inspiratory (room air) phases were executed via custom-made ‘breath tracker’ algorithm. Here, we used an endogenous VOC (e.g., acetone) with orders of magnitudes higher concentration in exhalation than in room air as the tracker mass.

Measured VOCs were quantified either via reaction rate coefficients (k-rates) between VOC and primary ion (at the E/N ratio of 140 Th) or via multi-component VOC standard mixture under matrix adapted conditions (breath humidity) by using a liquid calibration unit (LCU, Ionicon Analytik GmbH, Innsbruck, Austria). Isoprene was quantified via LCU based calibrations.

Results

Amongst 2000 subjects from consecutive clinical screenings, we obtained only five (3 females and 2 males) isoprene absent healthy adults (i.e., rare with <0.03% prevalence), 64 (39 females and 25 males) isoprene deficient (with low exhaled concentrations <50 ppbV) adults and 1318 (687 females and 631 males) isoprene normal (i.e., exhaled concentrations >50 ppbV) adults aged between 20 – 60 years. Besides, we obtained 345 (158 females and 187 males) subjects aged between 01 – 19 years and 268 (196 females and 72 males) subjects aged between 61 – 90 years [8].

Amongst all homozygous (100% allele frequency) mutations with <1% European prevalence, an isopentenyl-diphosphate delta isomerase-2 (*IDI2*) stop-gain mutation was shared between the rare adults revealing the genetic origin of isoprene absence. This mutation caused losses of enzyme active sites and affected the magnesium ion–cofactor binding sites. *IDI2* variant was heterozygous in their isoprene deficient family members and was absent in unrelated adults. No considerable serological aberration or mutation was found in the isoform *IDI1* in any participant [8].

Human *IDI2* is highly expressed only within the peroxisome (lipolytic organelle) of skeletal-myocytes, while expression of *IDI1* is conserved in various tissues and mainly in the liver. Although, *IDI1* may produce some amount of isoprene in the liver, cytochrome-P450 enzymes of human hepatocellular microsomes immediately oxidize isoprene. Preclinical studies have shown that unlike other mammals, pigs and bottle-nose dolphins do not exhale isoprene. We searched and found that these animals do not express *IDI2 [*8*]*.

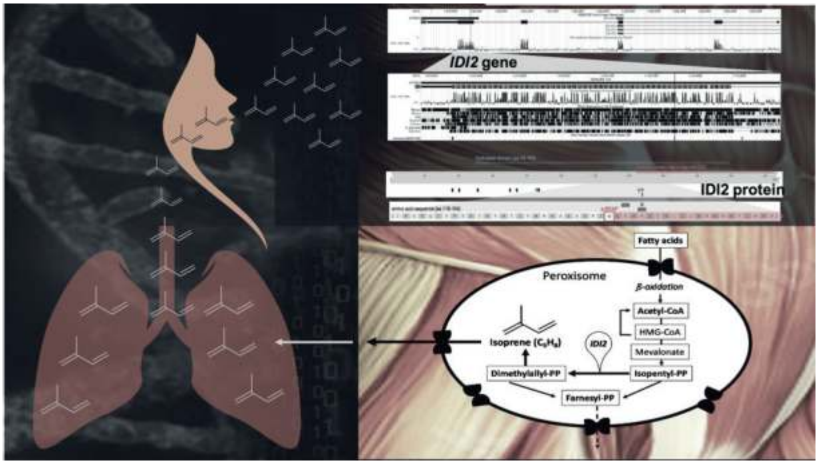

Figure 1: IDI2 gene expression in human skeletal-muscular peroxisome leading towards isoprene synthesis and continuous release via exhaled breath. Mutation in IDI2 gene (rs1044261 variant at p.Trp144Stop) causing aberration in IDI2 *protein structure and thereby, resulting in losses of enzyme active sites and metal co-factor binding sites. Thus, isoprene is absent in subject with IDI2 mutation.*

Discussion

Skeletal muscles metabolize lipids (oxidize cholesterol and fatty acids) to produce energy, regulate intramyocellular signaling and integrity. Beta-oxidation in myocellular peroxisomes produces acetyl-CoA i.e., channeled towards dimethylallyl diphosphate [(C_{14})DMAPP] production. As human *IDI2* catalyzes the isomerization of isopentenyl diphosphate [(C_{14})IPP] to highly nucleophilic DMAPP the origin of human isoprene is related to muscular metabolism rather than the suggested cholesterogenesis in the liver [8].

The well-known instant rise in breath isoprene during muscle activity (movement/exercise) along with our present findings underpin its actual origin from lipolysis in the skeletal muscles. In plants, only DMAPP is converted to isoprene via isoprene synthase enzyme. As humans do not have isoprene synthase or its enzyme homologues, the wild type *IDI2* gene and enzyme turned out as the rate limiting factor for human isoprene production [8].

Our discovery of the genetic origin and metabolic routes of human isoprene production enabled objective interpretations and applications of isoprene as a noninvasive biomarker for various conditions of clinical interest and elucidated new frontiers in sports and musculoskeletal medicine.

Knowledge of accurate metabolic origin is indispensable for valid clinical interpretation of any endogenous biomarker. Apart from isoprene, our breath contains many potentially endogenous VOCs and their sources are yet uncertain. We cannot speculate on clinical outcomes based on putative substance origins as such practice inevitably is prone to error.

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Applications in the Industry

Monitoring of the airborne molecular contamination (AMC) in a semiconductor factory with a PTR-TOF-MS

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Abstract

In a semiconductor factory, airborne molecular contamination (AMC) can lead to serious defect on either the product itself (electronic chips) or on production tools. To prevent such issues and possible production loss, we must monitor closely and continuously the molecular contamination in the most critical production areas (photolithography) and inside critical tools to detect quasi-instantly any drift of our baselines and, in-fine, identify and contain sources of contamination.

Introduction

Airborne molecular contamination is defined by all contaminants such as volatile organic compounds (VOC), acids (acetic acid, hydrofluoric acid, hydrochloric acid, …) and bases (ammonia, sodium). Those contaminants come from various sources such as human activities, processes, chemical products used along the production process and their by-products and must be kept at sub-ppbv (parts per billion per volume) levels in the most critical production areas and even lower inside the most critical equipment.

Conventional solutions like Tenax TA for VOC and bubbling systems for organic acids do not allow to reach detection limits as low as those required by the semiconductor activity for all critical contaminants. They also cannot be effective solutions for a continuous monitoring of airborne molecular contaminations.

PTR-TOF-MS on the other hand has the analytical capabilities to answer to most of our needs as it allows a monitoring of a large range of compounds with a detection limit as low as 0,01 ppbv. When coupled to a sequencer, it makes it possible to closely monitor our baselines over a large factory area. The real interest of the PTR-TOF-MS is revealed when it is used to monitor the efficiency of filtering units used to clean the air of production areas and inside tools or to identify sources of contamination such as leaking pipes or broken parts.

Experimental Methods

A PTR-TOF-MS serie 1000 is coupled with a sequencer to monitor 64 different points within the production area. A specific library made of the most critical compounds for our activity is used to monitor simultaneously a large range of families such as oxygenated, fluorinated, amines, aromatics, organic acids, condensable (boiling point > 150°C) and non-condensable (boiling point < 150°C) …. For each monitored point, specification limits are defined for each compound according to either the literature or our historical baselines.

The aim of this setup is:

1: Monitor the filtration efficiency of units used to clean the air inside the production area (Figure 1)

2: Monitor the filtration efficiency of units in place inside some production tools to add a second stage of filtration (Figure 2)

3: Control baselines according to current specification limits

4: Detect any airborne molecular contamination event due to potential leakages or broken parts (Figure 3 & 4)

To perform this monitoring, we use a specific measurement recipe focused on the most critical points of the production area. As soon as a measurement triggers a specification limit defined for one of the contaminants, an automatic alert is sent so actions can be initiated while the analyzer/sequencer automatically switches to a specific measurement recipe defined to secure the production area where the contamination has been detected.

Results

In a semiconductor factory, the air is continuously cleaned to maintain the airborne molecular contamination at levels in agreement with the quality needs of the manufactured products. To do so, the factory is divided into three different parts (Figure 1):

- The plenum, above the production area
- The production area, commonly called the “clean room”
- The basement, below the production area

In this configuration, the air goes from the top (plenum) to the bottom (basement) and is then sent back to the plenum through cleaning units where chemical filters retain all contaminants (VOC, acids & bases).

For the most critical processes, an additional step of chemical filtration is placed on the equipment.

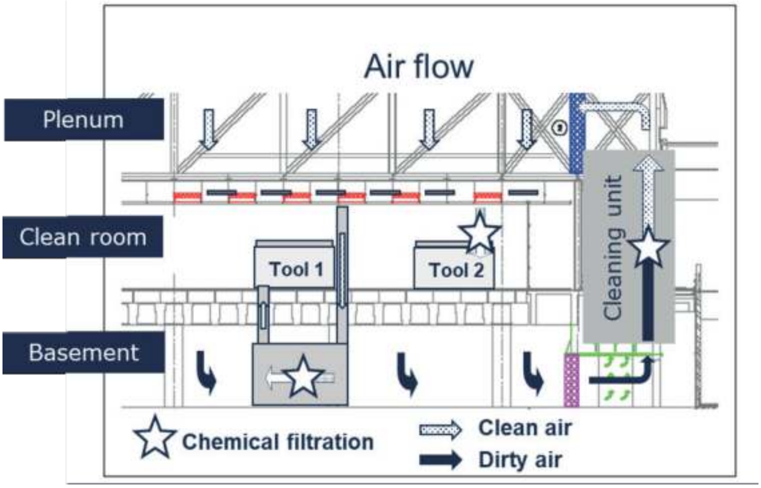

Figure 1: Configuration of a semiconductor factory

Figure 2 shows, for one area of the factory, an example of the airborne molecular contamination measured for a given contaminant in the basement, the plenum & inside an equipment.

We can see:

- The level of contamination measured before the first stage of filtration (= basement)
- The level of contamination measured after the first stage of filtration (= plenum)
- The level of contamination measured after the second stage of filtration (= inside an equipment)

The graph reveals reduced levels of contamination after each stage of filtration. In this specific example, and for this specific contaminant, chemical filters are still efficient with an filtration efficiency of over 60% for the first stage of filtration (basement to plenum) and of almost 100% for the second stage in the equipment.

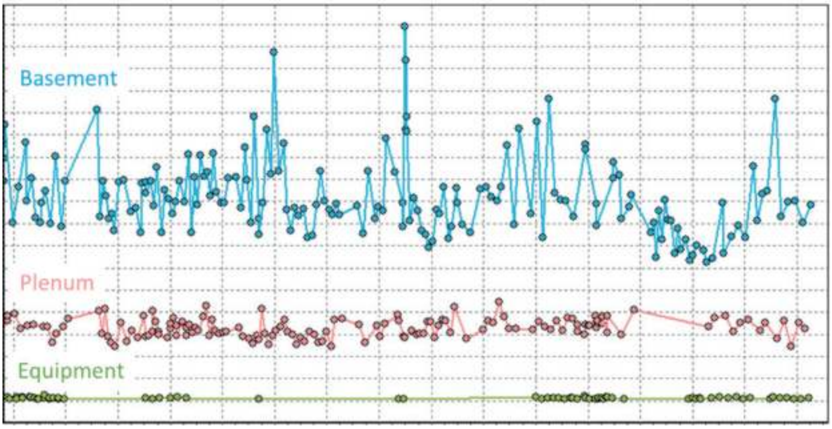

Figure 2: Monitoring of cleaning units in place to clean the air of the production area and inside a critical tool used in photolithography

In any factory, aging facilities can lead to possible leakages that will contaminate the air of the production area and, in some cases, impact the product and/or the equipment.

Figures 3 & 4 show how the PTR-TOF-MS was able to detect two different contaminations in one of our production areas. In both cases, the detection led to an automatic alert and specific investigations have been conducted to identify and contain the sources of those contaminations within hours.

Figure 3 shows a 1-methoxy-2-propanol acetate (PGMEA) contamination due to a broken part in a photolithography equipment which used a resist made of this contaminant. To solve this leakage, a first repairs has been done on the broken part but didn't last. As a consequence, the PGMEA contamination rose back to its initial level of contamination (Repairs # 1 on Figure 3). The replacement of the part by a new one was here the effective solution to solve the event with an instant drop of the PGMEA contamination (Repairs # 2 on Figure 3).

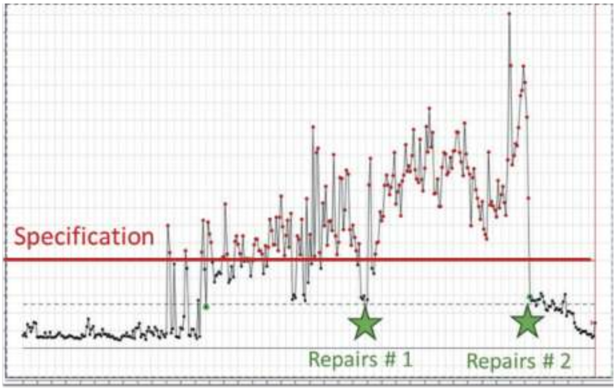

Figure 3: PGMEA contamination detected with the PTR-TOF-MS

Figure 4 shows a Trimethylsilanol (TMSOH) contamination alongside an ammonia (NH3) contamination, both detected simultaneously by our analyzers (PTR-TOF-MS and Analyzer #2). In this specific case, we focused our investigations on a possible Hexamethyldisilazane (HMDS) leakage as this solvent is known to produce, by a hydrolysis reaction, TMSOH and ammonia (HMDS => 2 TMSOH + NH3).

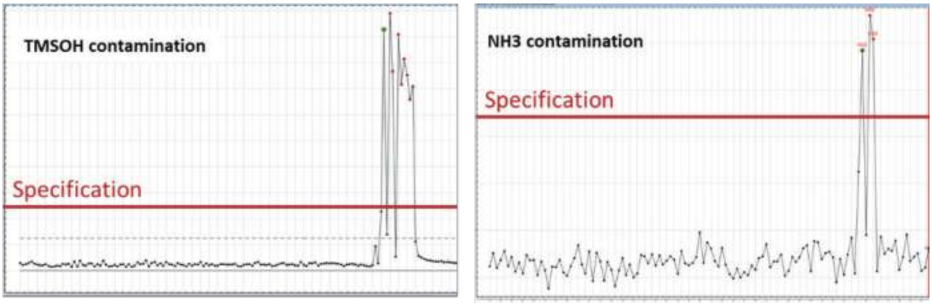

Figure 4: TMSOH & NH3 contamination simultaneously detected with the PTR-TOF-MS & the Analyzer #2

Discussion

In a semiconductor factory, airborne molecular contamination needs to be closely monitored and kept under restrictive specifications to avoid non-reversible impact on manufactured products or damages on facilities. To address such constraints, the use of the PTR-TOF-MS comes as one of the best solutions as it allows a monitoring of a large range of compounds, over a large range of chemical families and through a large range of concentrations from 0,01 ppbv to hundreds of ppbv. The use of this analyzer, when coupled to a sequencer, gives use the possibility to monitor continuously airborne molecular contamination over all critical areas and equipment of the factory, to maintain our baselines, and mostly, to detect, identify and solve any source of chemical contamination in hours thanks to a live monitoring instead of days or months with the use of conventional solutions.

From a customer perspective, the last step to be able to use all the capabilities of the PTR-TOF-MS is to be self-sufficient for a post-analysis of the data to identify unknown contaminants.

From Lab to Fab - Enhancing PTR-TOF for Industrial Monitoring

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Abstract

"From Lab to Fab" outlines the process of transforming a PTR-TOF from a scientific analyzer into an automated monitoring system. Strategic additions in hardware and software have culminated in a version of PTR-TOF specialized for industrial monitoring. We provide an overview of its current applications and present a performance assessment, including recent enhancements. Some of the implemented features could also be valuable for scientific campaigns requiring high stability or a large degree of automation.

Introduction

Airborne Molecular Contamination (AMC) poses a significant challenge in clean production environments, impacting industries such as semiconductors, pharmaceuticals, and other highly pure production environments. Gaseous or vapor-phase contaminants, particularly Volatile Organic Compounds (VOCs), can lead to detrimental chemical modifications on product surfaces, such as micro-corrosion or oxidization. Monitoring and controlling contamination levels are crucial to maintaining product quality, performance, and yield in these sensitive environments [1].

Traditional monitoring methods, often offline and lacking the required sensitivity and time resolution for real-time measurements, fall short. Addressing these challenges calls for new monitoring technologies and methodologies that can provide rapid, accurate, and reliable AMC level measurements.

PTR-TOF is a highly sensitive analytical technique, known for its soft ionization and ultra-sensitive real-time analysis of VOCs. As a direct-injection method, it eliminates the need for pre-separation or pre-treatment steps and is therefore widely used in many areas of scientific research.

The use of PTR-TOF in industrial settings, such as AMC monitoring in semiconductor production, introduce new challenges. The need to measure a complex list of compounds, not all suitable for H3O+ ionization, requires collecting samples in multiple ionization modes. Additionally, the list often includes isomers that need separation, posing an intrinsic challenge for PTR-TOF. A full automation of the entire measurement and data evaluation process is imperative. The results have to be calculated in real-time, in contract to the often-retrospective data analysis in scientific campaigns. Moreover, unattended 24/7 operation over weeks sets high demands on the requires reliability and stability of the systems.

We present the steps "From Lab to Fab" that signifies PTR-TOF's transformation from a scientific analyzer to a valuable tool for automated industrial monitoring. We discuss modifications in hardware and software of an IONICON PTR-TOF system to meet the challenges required for automated industrial monitoring and give an overview of the current applications. Several of these improvements are also be relevant and applicable in scientific applications.

Experimental Methods

In the majority of industrial applications, PTR-TOF 1000 [2] is the preferred choice due to its affordability and unparalleled robustness. To facilitate the integration of PTR-TOF into analyzer cabinets, a more compact version has been designed with the standard width of 19”, a common format for rack integration. Despite this modification, it retains identical components and performance to the stand-alone versions of IONICON PTR-TOF.

The transformation "From Lab to Fab" initiates with essential modifications to the standard PTR-TOF hardware. A built-in industrial PC replaces conventional computing setups. This specialized PC operates on a tailored version of Windows 10 designed for industrial environments. Unlike regular systems, it avoids unscheduled updates that could disrupt continuous measurements. Additionally, power-saving settings, often implicated in connection interruptions, are disabled. This upgrade ensures the stability and reliability required for seamless operation in industrial applications.

Other hardware modifications include the addition of a multiport valve inside the heated inlet chamber that allows to select between different inlet ports. Even if only one sample stream is to be measured, this is a useful addition, to select a closed port for remote standby or shutdown. Another port is connected to an Internal Calibration System [3] (ICS), that allows to switch to defined concentration levels for system check and automated calibration measurements, as well as to measure clean air (zero-air) as a background measurement.

The development of the Automated Measurement and data Evaluation (AME) software [4] was a crucial step for the implementation of PTR-TOF technology as an industrial monitoring solution. AME automates both the measurement and data evaluation, enabling unattended, continuous monitoring by automatically cycling through different ionization modes and consolidating averaged data for evaluation. The evaluation can consist of simple strategies to select the optimal m/z in a respective mode to measure a compound, or multiple signals can be added to display sum values, e.g. Total VOC. For enhanced data evaluation, the AME software uses compound libraries in combination with pattern fitting algorithms to extract the concentration of compounds of interest with enhanced specificity and the ability to separate isomers and interferences. The ability to seamlessly correlate data of different ionization modes extends the capabilities beyond the normal use of PTR data. A simple, user-friendly interface enables operators with no prior knowledge of PTR-MS to easily select measurement recipes, view concentration values, and set alarm levels. AME concentration data is stored in accessible ASCII tables and can be accessed online through a MODBUS over TCP interface.

This journey ‘From Lab to Fab’ has culminated in Version 1.0 (V1.0) of our industrial PTR-TOF 1000 in the 19” rack-mountable version with the described hardware and software enhancements. These systems have been intensively tested in the field, most of them for monitoring in semiconductor production. This provided valuable input that allowed a customer driven improvement process to address specific challenges.

To enhance the AME software's capabilities, a new feature called "Actions" was introduced. This enables the execution of specific tasks in synchronization with the cycling of ionization modes. It allows for seamless acquisition of new backgrounds without disrupting the cycling process, and facilitates efficient switching between different sampling lines. Additionally, the most frequently performed task of tuning the Micro-Channel Plate detector setpoint (MCP-B) has been fully automated within the measurement process. Software enhancements can easily be retrofitted to existing systems.

This is not the case for improvements that involve hardware, which not only need to comply with high standards but are also evaluated for the possibility to modify existing systems. Two hardware improvements directly address shortcomings identified in the field. These include the introduction of the fastSRI ion-source and a modified drift tube “EVR-X” and we will present a comparison between the V1.0 and V1.5, which includes these improvements.

To assess the performance of these systems we use a gas standard (IONICON SEMImix) with 11 components, relevant to the Semiconductor industry.

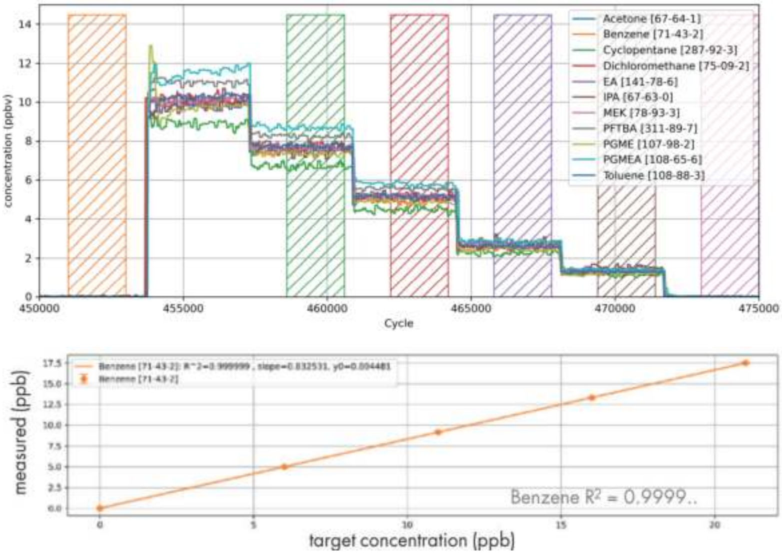


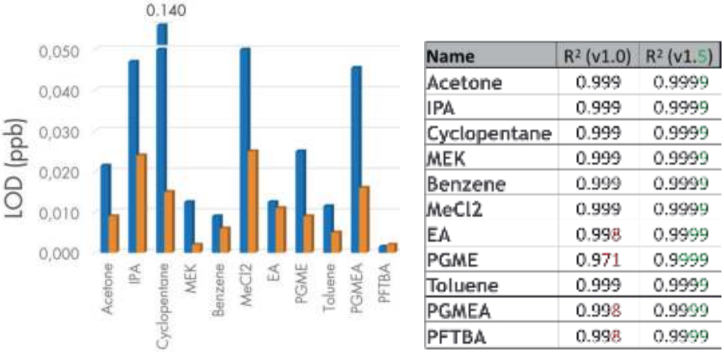
Figure 1: (upper) Typical calibration measurement with SEMImix gas standard, ICS and results calculated by AME. The hatched areas are averaged to produce a calibration plot (lower).

Connected to the ICS the standard can be diluted to different concentration levels. The linearity can be determined with a series of calibration steps, see Figure 1. By repeatedly measuring a specific calibration step we can demonstrate the systems stability. The LOD is calculated as 3 times the standard deviation of the 0 ppb step.

Results and Discussion

The first PTR-TOF for industrial monitoring have been deployed to the field in 2018. To date, over 100 such systems are operational, effectively showcasing their efficacy. The main area of within industrial applications is in semiconductor manufacturing and for example provide monitoring of AMC concentrations in different sampling locations [5] and monitoring the contamination levels in transport containers for wafers [6]. In both cases the PTR-TOF are integrated into larger analyzer cabinets. Moreover, also manufacturers of lithography tools, and producers of filter systems for semiconductor employ PTR-TOF to assess contamination levels.

The implementation of the fastSRI ion-source and the EVR-X drift chamber (in V1.5), have further enhanced the systems linearity and limits of detection (LOD), see Figure 2. The presented software enhancements, the automated (scheduled) MCP-B tuning and background measurement, had a positive impact on the long-term stability which is particularly important for unattended monitoring.



Name	R^2 (v1.0)	R^2 (v1.5)
Acetone	0.999	0.9999
IPA	0.999	0.9999
Cyclopentane	0.999	0.9999
MEK	0.999	0.9999
Benzene	0.999	0.9999
MeCl2	0.999	0.9999
EA	0.998	0.9999
PGME	0.971	0.9999
Toluene	0.999	0.9999
PGMEA	0.998	0.9999
PFTBA	0.998	0.9999

Figure 2: Comparison of the LOD of V1.0 (left, blue) vs. V1.5 (right bar, orange). (right) Improvement in Linearity measured by R^2.

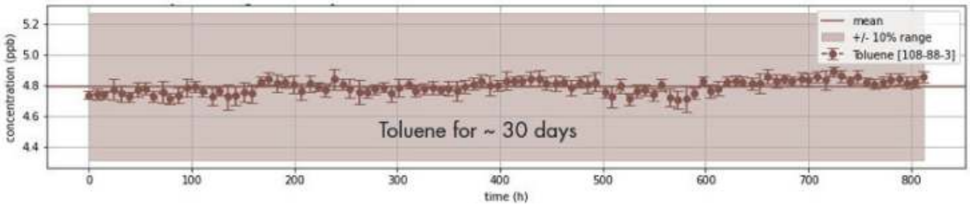


Figure 3: Repeated measurement of 4.8 ppb of Toluene, for 800 hours, to demonstrate the stability.

This can nicely be demonstrated using stability measurements, see Figure 3.

In summary, the robust hardware, automated processes, and continuous refinement pave the way for a new era in automated real-time VOC monitoring, demonstrating the successful transition of PTR-TOF "From Lab to Fab."

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Trace gas analysis with PTR-MS at Carl Zeiss SMT for quality control of Deep UV optical lithography systems

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Abstract

Organic contamination inside optical systems of semiconductor lithography tools could lead to transmission loss, lens heating issues or complete failure of the system. Quality control measurement after production and assembly are mandatory, however, also time critical in serial production. We present a novel approach for online acceptance measurements of deep ultraviolet photo lithography equipment using PTR-MS.

Introduction

Until now TENAX analytics has been used for detection of volatile and non-volatile organics in gases. This method has several disadvantages: online analysis is impossible (takes at least 2 days) and large sample volumes are needed for low limits of detection. Because of these drawbacks a novel approach for the routine analysis of optical systems was needed. The application of *P*roton *T*ransfer Reaction *T*ime *o*f *F*light *M*ass *S*pectrometry (PTR-TOF MS) delivers fast results and allows for online quantification of gaseous contaminations.

Experimental Methods

PTR-MS uses soft ionization technology with low fragmentation rates. By proton transfer from H_3O^+, all compounds with a higher proton affinity (PA) than water get ionized (this means almost all organic substances!). Common constituents of air, such as N_2, O_2, Ar, CO_2 etc. have lower PAs than H_2O and are therefore not detected and do not disturb the measurement. Due to precisely controlled ion source and drift tube parameters, absolute quantification of VOC (*v*olatile *o*rganic *c*ompounds) concentrations is possible. Not only trace volatile organic compounds are detected by PTR TOF-MS but additionally also very important, inorganic substances can be detected and quantified with the same instrument. As all ionizing agents are produced in a hollow cathode discharge ion source with good purity no additional mass filter is needed for reagent ion selection (as in other analytical methods employed) and remaining reagent ion impurities can be clearly distinguished from isobaric sample compounds due to the high mass resolution of the time-of-flight mass spectrometer used.

Results

PTR-MS is used for quantification of gaseous contaminants inside optical tools. With its high sensitivity and fast answer times it is well suited for routine quality control of DUV (deep ultraviolet) lithography optics. To make it applicable in a serial manufacturing process, we developed a software-based user interface, making PTR-MS accessible for non-scientists. After connecting the DUV optic to flow and PTR-MS, the operator can start the measurement by simply pushing a button. Analysis is facilitated by a traffic light system: The response of ‘green light’ directly allows the operator to ship the system to our customer, while remaining ‘red’, the system is not sufficiently flushed yet or requires for consultation of first or second level support. Only in this case the development department or head of production, who are intensively trained on PTR-MS is contacted.

Implementation of this process enables faster shipping (substantial time saving) and additionally decreases unnecessary coverage of valuable clean room space. The process might be expanded to other manufacturing applications in our company.

Figure 1: Two ZEISS employees handling a DUV photo lithography optic. The optics final quality control for volatile contaminants is carried out with PTR-MS

Instruments & Technology and Future Trend

Analyzing PFAS via SRI-PTR-MS

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Abstract

In this preliminary study the capability of analyzing Poly- and Perfluoroalkyl Substances (PFAS) using Switchable-Reagent-Ion Proton-Transfer-Reaction Mass Spectrometry (SRI-PTR-MS) is presented. Several different subtypes and relevant representatives of this compound class were investigated for this purpose. Reflecting their chemical diversity, various ionization and reaction pathways can be used to analyze these compounds. The persistence of PFAS in indoor air is demonstrated in a proof-of-concept study.

Introduction

The chemical industry provides a large class of thousands of synthetic chemicals, PFAS, which have exceptional properties. These properties are partly due to the stability of the carbon-fluorine bond. The problem is that nature is unable to break this bond, so many of these compounds are ubiquitous and have been labelled “forever chemicals”. They are associated with serious health concerns and are therefore subject to increasingly stringent restrictions. Many of these compounds have been added to the European Chemicals Agency’s (ECHA) Candidate List of substances of very high concern [1]. Some countries even are discussing a complete ban on the use of PFAS. The detection and quantification of PFAS has recently become one of the hottest topics in analytical chemistry. So far, the vast majority of analytical studies of PFAS have been conducted offline, using the gold-standard but time-consuming GC- and LC-based techniques [2]. Here we present preliminary results from a comprehensive series of real-time direct injection PTR-MS studies on PFAS: experimentally determined Limits-of-Detection (LoDs), insights into the ion chemistry and a proof-of-concept indoor air study.

Experimental Methods

A PTR-TOF 6000 equipped with SRI capability was utilized for this purpose [3,4]. H_3O^+, NO^+, O_2^+ and NH_4^+ were used as reagent ions and reduced drift field strength settings are optimized for maximum sensitivity and specificity in the analysis of PFAS. Perfluorotributylamine (PFTBA, $C_{12}F_{27}N$) was available as a gas standard for calibration purposes. All other chemicals were purchased in highest available purities from Merck, Apollo Scientific, Carl Roth, Santa Cruz Biotechnology, HPC Standards or Fisher Scientific. Generated gas phase concentrations were subsequently analyzed in an automated sequence using different primary ions.

Results

In the first part of this study, we investigated the LoD for this class of compounds. Dissociative PTR reactions of H_3O^+ with PFTBA result in a main product ion at m/z 413.977 ($C_8NF_{16}^+$). By diluting the gas standard, we were able to determine LoDs of 2.9 pptv and 340 ppqv for 1 s and 1 min integration time, respectively. The resulting sensitivity of this compound of 2018 cps/ppb (25 kHz) is comparable to other compounds used to calibrate of a PTR-TOF instrument in identical mass regimes.

Several well-known PFAS were tested and showed distinct reactivity towards different primary ions. None of the investigated compounds showed any reactivity towards NH_4^+ ions, regardless of the applied drift field voltage. Table 1 provides a simplified overview of the main reaction channels, resulting masses and their corresponding tentatively assigned ions. However, polyfluorinated acids are only ionized in O_2^+ mode, with fragmentation leading to either $C_3F_6^+$ or $C_3F_5^+$. A sum parameter can be introduced for such compounds. The unambiguous identification of other compounds is possible due to their clear reactivity in different modes.

Abbreviation	Compound	Sum Formula	Isotopic Mass	Ion (O_2^+)	m/z	Ion (H_3O^+)	m/z	Ion (NO^+)	m/z
PFBA	Perfluorbutanoic acid	$C_4HF_7O_2$	213.986	$C_3F_6^+$	150				
PFPeA	Perfluorpentanoic acid	$C_5HF_9O_2$	263.983	$C_3F_5^+$	131				
PFHxA	Perfluorhexanoic acid	$C_6HF_{11}O_2$	313.980	$C_3F_5^+$	131				
PFHpA	Perflorheptanoic acid	$C_7HF_{13}O_2$	363.977	$C_3F_6^+$	150				
PFOA	Perfluoroctanoic acid	$C_8HF_{15}O_2$	416.981	$C_3F_5^+$	131				
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	513.967	$C_3F_5^+$	131				
FOSA	Perfluoroctanesulfonamide	$C_8H_2F_{17}NO_2S$	498.953	$H_2NSO_2^+$	80			$[M{\cdot}NO]^+$	529
6:2 FTOH	2-Perfluorohexyl ethanol	$C_8H_5F_{13}O$	364.013	$C_4H_3F_4^+$	127	$[M{\cdot}H_3O]^+$	383	$[M{\cdot}NO]^+$	394
8:2 FTOH	2-Perfluorooctyl ethanol	$C_{10}H_5F_{17}O$	464.007	$C_4H_3F_4^+$	127	$[M{\cdot}H_3O]^+$	483	$[M{\cdot}NO]^+$	494
10:2 FTOH	2-Perfluorodecyl ethanol	$C_{12}H_5F_{21}O$	564.001	$C_4H_3F_4^+$	127	$[M{\cdot}H_3O]^+$	583	$[M{\cdot}NO]^+$	594
GenX	Perfluoro(2-methyl-3-oxahexanoic) acid	$C_6HF_{11}O_3$	329.975	$C_5OF_{10}^+$	266				
8:2FTAcr	1H,1H,2H,2H-Perfluordecyl-acrylat	$C_{13}H_7F_{17}O_2$	518.170	M^+	518	$[MH]^+$	519	$[M{\cdot}NO]^+$	548
-	1H,1H,2H,2H-Perfluorhexylmethacrylate	$C_{10}H_9F_9O_2$	332.046	M^+	332	$[MH]^+$	333	$[M{\cdot}NO]^+$	363
-	1H,1H,2H-Nonafluorhexyl-1-ene	$C_6H_3F_9$	246.009	$C_3H_3F_2^+$	77	$[M-F]^+$	227		

Table 1: Simplified overview of several PFAS investigated via SRI-PTR-MS. Only main signals are listed herein.

As an example, Figure 1 shows a mass spectrum of the compound 8:2FTAcr and its typical reaction channels for the different primary ions used. Provided that the relevant reaction pathways are understood, this can greatly enhance selectivity.

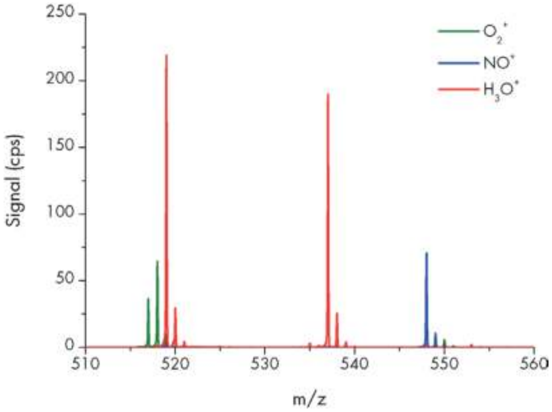

Figure 1: Mass spectra of 8:2FTAcr ionized via O_2^+, H_3O^+ and NO^+. Average mass spectra for each ionization mode are shown in different colours. Main ions found for each channel are M^+ for O_2^+ (green line), MH^+ and $[M{\cdot}H_3O]^+$ for H_3O^+ (red line) and $[M{\cdot}NO]^+$ for NO^+ (blue line).

We analyzed the indoor air quality of a 30 m³ office room with low ventilation. The focus was on monitoring the persistence of PFBA in the air after its release at levels of a few ppbv. PFBA is known to accumulate in the lungs, and elevated plasma levels are associated with a more severe COVID-19 prognosis [5]. The study involved a weekend measurement of heptafluorobutyric acid, Figure 2. Initial concentration of 676 ppt due to evaporation from a Petri dish distributed in the room with a fan. After about 9 minutes, the fan was switched off and no increase was seen as the room was warmed by sunlight. After 1 hour, the concentration was at 6 pptv, i.e. approximately at background level.

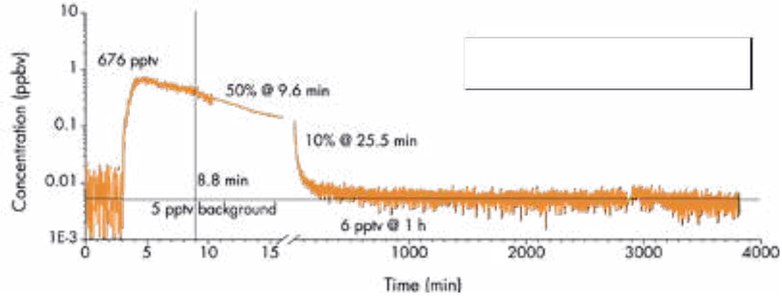

Figure 2: Weekend measurement of heptafluorobutyric acid

Discussion

The use of SRI-PTR-MS has some limitations and cannot be considered a universal method for analyzing all types of PFAS. However, it has been demonstrated to be applicable in real-time for a wide range of PFAS, with detection limits as low as pptv levels.

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Introducing IDA, a powerful and fast data analysis suite

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Abstract

State-of-the-art time-of-flight mass spectrometers serve as the analytical heart of current IONICON PTR-MS instruments. These high time- and mass-resolving TOF-MS are capable of generating gigabytes of data per hour that contain all the desired information including exact mass-over-charges and temporal variations of hundreds of detected ions. With the IONCION Data Analyzer (IDA) we have recently introduced a new platform to visualize, analyze and manage IONICON TOF-MS projects.

IDA is the ideal software for all PTR-MS users, from beginner level to expert, that seek to extract the most of their large datasets in a reasonable time without significant amounts of manual labor. IDA offers a user-friendly interface with dynamic elements to focus on relevant tasks only. This modern appearance is combined with state-of-the-art data analysis algorithms that offer a quick and reliable data analysis progress [1-3].

IDA's data reduction includes software assisted tools for mass axis re-calibration, peak-shape calculation, mass resolution determination and a full baseline correction based on your data-acquisition time. IDA provides software solutions for a targeted and untargeted high resolution peak analysis including an automatic isobaric peak deconvolution and an assignment to chemical compositions based on exact masses and isotopic distribution patterns (see Figure 1). Quantify your data with a series of dedicated software tools and benefit from IONICON's more than two decades of experience in ion chemistry.

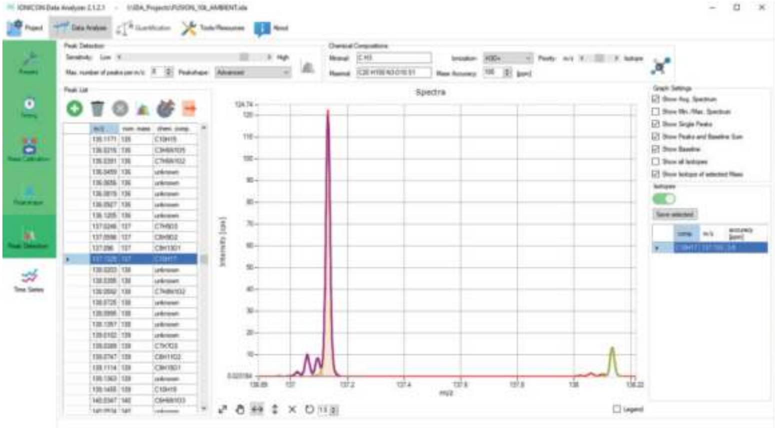

Figure 1: IDA's Peak Detection tool automatically separates peak-systems to individual detected ions and assigns chemical compositions based on exact m/z and isotopic patterns.

In this presentation we summarize the capabilities of IDA and demonstrate its unique performance to analyze large datasets containing hundreds of peaks in short amounts of time.

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Characterization and application of an ultrahigh sensitivity PTR-MS instrument with a well-defined ion chemistry

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Abstract

We present a novel instrument for detecting organic compounds on a molecular composition level in real-time based on proton-transfer-reaction mass spectrometry (PTR-MS). This FUSION PTR-TOF 10k combines several improvements compared to state-of-the-art PTR-MS technology:

An optimized Fast-SRI (selective reagent ion) ion source is capable of switching between four ionization modes with H_3O^+, NH_4^+, NO^+, and O_2^+ primary reagent ions within sub-seconds to seconds. In addition, this new ion source improves the decoupling from the reaction chamber providing lowest interferences with neutral radicals (e.g. OH < 0.1%) and parasitic reagent ions (< 2% for all ionization modes). Table 1 summarizes the primary reagent ion purity for all ionization modes.

Table 1. Overview of the impurities of the primary reagent ions (PI; H_3O^+, NH_4^+, NO^+, and O_2^+) in percent.

PI-Mode	H_3O^+	NO^+	O_2^+	NH_4^+
H_3O^+-Mode	98.64	0.49	0.83	0.03
NO^+-Mode	0.63	99.20	0.17	0.00
O_2^+-Mode	0.25	1.50	98.25	0.00
NH_4^+-Mode	1.44	0.37	0.12	98.07

Ion-molecule reactions with organics occur in a fully-controlled environment of a novel reaction chamber called FUSION where a traditional DC drift field can be superimposed by RF voltage. FUSION provides the needed clean ion chemistry with ion-molecule reactions at predictable reaction energies and reaction rates that are crucial for quantitative operation of a PTR-MS.

This FUSION RF reactor is coupled to a high duty-cycle PTR-TOF mass spectrometer with a rated mass resolution m/dm > 10 000. This allows for a good separation of isobaric signals and an unbiased assignment of most chemical compositions of interest.

With these enhancements, FUSION PTR-TOF 10k achieves lowest limits of detection (< 1 pptV in 1 s) and sensitivities up to 80 000 cps $ppbV^{-1}$ while conserving the clean ion chemistry, linear response and soft ionization settings of a traditional PTR-MS. A schematic of the instrument is depicted in Figure 1.

To demonstrate the unique capabilities of FUSION PTR-TOF 10k two experiments were performed: (1) a CHARON particle inlet is coupled to the instrument to measure fresh secondary organic aerosol (SOA) from the ozonolysis of limonene, and (2) a measurement of ambient air in Innsbruck, Austria, to demonstrate the linear response to clear sub-pptV levels (Figure 2).

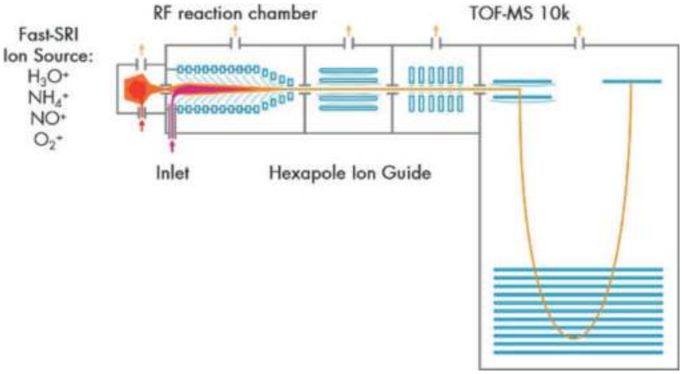

Figure 1: Schematic of the FUSION PTR-TOF 10k.

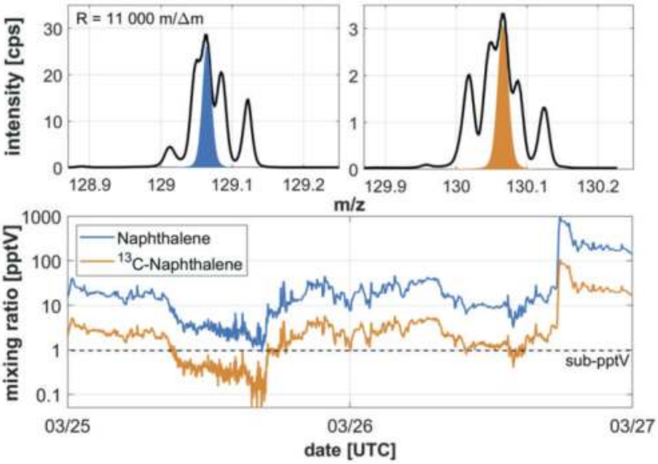

Figure 2: Time-series of naphthalene in ambient air in Innsbruck, Austria, including its ^{13}C isotope demonstrating a linear response down to clear sub-pptV levels.

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From metallurgical gases towards green hydrogen. PTR-TOF-MS - a remarkable companion of the energy transition and defossilization

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Abstract

After our previous studies understanding the artifacts and dynamics in the background of diluting gases used in the characterization of industrial gases, we present a detailed analysis of the most challenging metallurgical gas, coke oven gas (COG), using a commercial Proton-transfer-reaction Quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF). A meticulous analysis was carried out for the assignment of 1306 peaks found in the PTR-TOF-MS mass spectrum, resulting in the tentative identification of more than 500 components in industrial COG, which will help in its application in a circular economy at steel mill plants. Regarding the number of peaks, hydrocarbons appeared as the main compound class (31.3%) followed by oxygen-containing (non-metallic) species (20.8%). In terms of intensity, hydrocarbons contributed with 79.82% followed by nitrogen-containing species with 13.79%. Critical compounds, such as sulfur species exhibited only 3.28% of the total ion signal. In order to validate the peak assignment, a Kendrick mass defect analysis was carried out, which showed an excellent agreement, despite the middle-range mass resolution of the PTR-QiTOF and helped to distinguish isobaric ions and previously unidentified peaks. This procedure will be applied in the analysis of green hydrogen in order to determine fingerprints and thus, support its application in the current energy transition in Germany.

Introduction

A clear commitment towards a CO_2 circular economy and a transition to low-emission energy carries (e.g. green hydrogen) obtained from renewable sources of energy are pursued in Germany with for instance the Carbon2Chem® project [1] and the new hydrogen roadmap. Contemporary infrastructure strongly depends on steel production, which is primary done via the carbon-intensive blast furnace converter route [1]. An alternative material, which could replace steel is not expected in the near future and the promising direct reduced iron (DRI) technology is still under development [2]. Although steel is highly recyclable, the steel demand is expected to increase due to the growing global population, leading to increased CO_2 emissions [3]. Current world-wide CO_2 emissions from the steel industry account for 6.7% [4].

Approaches such as Carbon Capture and Utilization (CCU) and the recycling of industrial waste gases can help mitigate the emission of greenhouse gases but it requires a profound knowledge of potentially damaging trace components, which even at the trace level can hinder the utilization of waste gases due to damages [5] (e.g. corrosion, abrasion) of downstream units or cause deactivation of catalysts in downstream processes, thus, resulting in higher operational costs. Therefore, the online characterization of trace components at the ppb/ppt level is necessary as input for the development of adequate purification processes. Usually, the online characterization of the metallurgical gases is limited to FTIR [6] or GC [7] analysis of the major compounds, whereas the trace compounds are only determined offline within certain time intervals [7]. PTR-TOF-MS has been successfully applied in the online analysis of metallurgical gases directly on-site at a steel mill plant of the company thyssenkrupp Steel Europe (tkSE) [8].

Experimental Methods

Site description

The PTR-measurements were carried out in the so-called HüGaProp (Hüttengas Properties) Lab-Container [8] at the steel mill plant of the tkSE located in Duisburg, Germany. Regarding the coke oven gas, the pipeline length from the sampling point to the coke oven plant was about 1,1-1,2 km. After conditioning in the pre-container, about 5 l min^{-1} of industrial gas is transferred to the HüGaProp Lab-Container through a ca. 10 m Teflon hose, which was also heated at 80 °C. Through a double bypass system, around 100 ml min^{-1} are transferred into a custom-made dilution box [8], in which a dilution with nitrogen 6.0 (purity $\geq$ 99.9999 %) in two steps takes place, before measuring with the PTR-QiTOF. The chosen dilution ratio of 1:600 was established using benzene as indicator, since it appeared as the most highly concentrate trace in COG.

PTR measurements

The measurements were performed using H_3O^+ as reagent ion. H_3O^+ ions are generated in the hollow cathode ion source using a water vapor flow of 7 sccm, in the PTR-QiTOF. The parameters for the drift tube were set to 900 V, 3.50 mbar and 60 °C, resulting in an *E/N* of about 131 Td. The inlet temperature was 100 °C. In the detection region, the instrument uses orthogonal acceleration in the V-mode. A mass range from *m/z* = 1 up to 797 was covered. The data acquisition per cycle was 1 s. The data presented are typically the average of four-hour measurements.

Data treatment and Kendrick mass defect analysis

Since the main goal of the non-target analysis of industrial COG was to identify all peaks in the PTR-TOF-MS mass spectra, no restrictions were made after the typical workflow suggested by IONICON for the subsequent Kendrick analysis regarding elements C, H, N, O, S, etc., the Ring and Double Bond Equivalent (RDBE) rule or the mass accuracy, which typically oscillated between -20 to 20 ppm for most VOCs with an average of 4 ppm counting after *m/z* 31. The introduction of the Kendrick mass (KM) [9] scale by choosing a CH_2 group (14.00000 u) as repeating unit opened the possibility to analyze homologous series in complex mass spectra by sorting them according to their Kendrick mass defect (KMD). This mass scale has become a standard protocol for the analysis of data obtained from ultrahigh-resolution MS in complex mixtures [9]. The Kendrick analysis was used to validate the assignment of the chemical formulas.

Results and Discussion

The PTR-TOF-MS analysis of industrial COG exhibited 1306 peaks and showed that the main compound class corresponds to hydrocarbons with 31.3% of all peaks in the mass spectrum and a contribution to the total ion signal of 79.82%. Aromatic and polyaromatic compounds appeared as the main hydrocarbons. In terms of abundance, nitrogen-containing ions followed with a contribution of 13.79% to the total ion signal but only with 7% of all measured peaks. Within this compound class, tentative assignments to amines, amides and nitriles were mainly made. Oxygen-containing trace compounds were assigned to 20.8% of all peaks and contributed to the total ion signal with 2.25%. The tentative assignment of these peaks was mainly made for ketones, aldehydes, furans, carboxylic acids and esters. Among potentially harmful compounds for the downstream catalysts used in the Carbon2Chem® project, such as sulfur-containing compounds, only a contribution of 3.28% to the total ion was observed. No volatile phosphorus-containing compounds were observed in the COG and only a few halogenated compounds could be determined with H_3O^+. Complementary measurements with the O_2^+ reagent ion would be necessary to get a broader picture of this complex gas matrix.

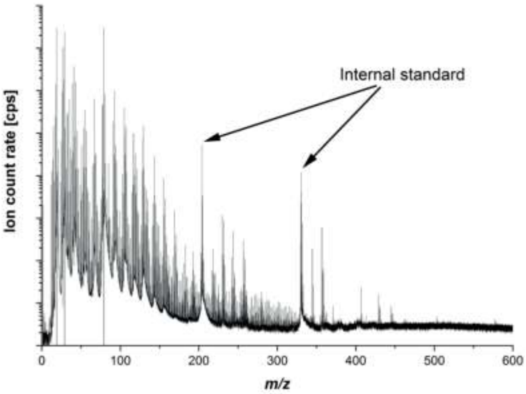

Figure 1: Mass spectrum of industrial COG measured online at the steel mill plant in a mobile container using H_3O^+ as the reagent ion with the PTR-QiTOF at E/N 131 Td.

A Kendrick mass analysis was performed to all 1306 peaks found in the industrial COG considering both, the theoretical exact masses and the experimentally determined, in order to check the peak assignment for consistency. The results showed an excellent agreement with the assigned compound classes. Additionally, a comparison with only the first isotopologues of the chemical formulas assigned from the full mass spectrum was made, showing a good agreement with the assignments of the second or third isotopologues despite the low intensities in some cases due to the strong dilution. This procedure will be applied in the analysis of green hydrogen in order to determine fingerprints and thus, support its application in the current energy transition in Germany.

Conclusions

It was shown, that PTR-TOF-MS is an excellent technique for the online gas analysis of complex industrial CO_2/H_2 sources like metallurgical gases. An almost complete picture of the composition of the trace compounds in COG down to the ppt-level has been obtained, which has not been achieved until now by any other technique. The assignment of the 1306 peaks found in COG was corroborated with the Kendrick mass defect analysis, which showed an excellent agreement even at moderate mass resolution. This procedure can be applied to other gas matrices such as green hydrogen.

Acknowledgments

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An Aerosol Thermal Desorption (ATD) inlet for the PTR3 mass spectrometer

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Abstract

Knowledge about the chemical composition of organic aerosols (OA) is of key importance in atmospheric research in order to understand the impact of OA on climate and health. The ATD inlet [1] addresses this challenge by utilizing infrared light to evaporate molecules from aerosol particles, followed by their analysis in the PTR3-TOF-MS [2]. This approach offers the advantage of minimizing particle contact with surfaces. In a first proof-of-concept study we analyzed outside air in Innsbruck. We detected signals of various C_2-C_8 compounds evaporated from outside air tropospheric particles. In the CLOUD chamber at CERN, the ATD inlet was tested in an experiment where Ultrafine particles were nucleated and grown from pure alpha-pinene oxidation. The experimental setup detected several oxidation products of alpha-pinene evaporated from particles under the influence of the infrared lamp. Consequently, our results confirm that the new inlet in combination with the PTR3-TOF-MS, proves effective in the analysis of OA, for compounds with a low number of carbon atoms.

Introduction

In recent years it became clear that Organic aerosols (OA) represent an important fraction of the aerosol mass. The atmospheric organic carbon budget is heavily influenced by the formation of secondary OA from gas-phase precursors. About 50% of submicron particles in the troposphere consists of organic mass [3]. A typical organic aerosol particle with a diameter of 200 nm contains 5–10 million individual organic molecules, with molar weights averaging around 200 g/mole [4].

Determining the chemical composition of OA still is a challenging task. More recent approaches combine chemical ionization mass spectrometry (CIMS) with special inlet designs. The “Filter Inlet for Gases and Aerosols” (FIGAERO) collects aerosol particles on to a filter, which then is heated and evaporated vapors are detected by a CIMS [5]. The CHARON "chemical analysis of aerosol online" uses a heated stainless steel capillary combined with a PTR-TOF MS [6]. The newly developed “Aerosol Thermal Desorption” (ATD) inlet aims to achieve this goal by heating aerosol particles with an infrared lamp, employing a heating mechanism, that does not involve surface contact. Evaporated vapors are then detected by a PTR3-TOF-MS.

Experimental setup

Figure 1 illustrates the components of the ATD inlet. A denuder eliminates volatile organic compounds (VOC) that would interfere with the aerosol measurements, as well as radicals such as O_3, ROx and HOx, reducing photochemistry induced by the IR-lamp. Following this, particles undergo thermal desorption for typically 0.4 seconds induce by heat radiation emitted by an infrared (IR) lamp. The light is focused onto a glass tube using an elliptical cavity, ensuring uniform irradiation of the particles [7]. This method minimizes surface-catalyzed reactions, which happen especially on stainless steel surfaces. Additionally, a bypass offers the flexibility to switch between aerosol and gas-phase measurements in the ATD inlet. The three measurement configurations: light mode (light on), denuder mode (light off), and gas mode (bypass) are repeatedly cycled through.

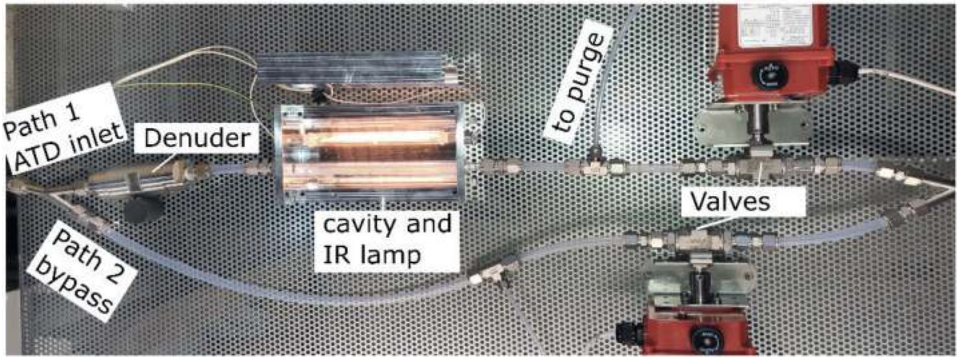

Figure 1: The ATD inlet consisting of a charcoal denuder, an IR lamp in an elliptical cavity, a second path as a bypass for gas phase measurements and two valves to switch between the two paths.

Results

The new ATD inlet system underwent testing by measuring ambient air just outside of the laboratory in Innsbruck, Technikerstraße 25 from Tuesday, March 1st, 9:00, until Wednesday, March 2nd, 13:00. Within 20 m distance from the sample inlet point a grove and various physics and biology laboratories are located, including a workshop. A street used by cars runs at a distance of ca. 80 m, while further away, at a distance exceeding 150 m, residential homes are located. The runway of the Innsbruck airport is located more than 500 m away.

Filtering the spectrum for peaks exhibiting significant difference between light and denuder mode yields a list of exact mass peaks, among which the mass m/z = 124.076 Th ($C_7H_9O\text{-}NH_4^+$) stands out prominently. We tentatively assign this sum formula to benzaldehyde. In Figure 2A, the signal of $C_7H_9O\text{-}NH_4^+$ is illustrated over two complete measurement cycles, with different measurement modes represented by distinct background colors (blue = gas, yellow = light, green = denuder). The pink curve depicts the temperature in the cavity with the infrared lamp, measured directly at the glass tube. In the light mode, the temperature in the cavity reaches approximately 180 °C. In the denuder mode, when the light is turned off, the temperature decays exponentially with a half-life of 2.4 min, reaching a temperature of about 33 °C. Mean values of the measurement points during the different modes are presented in Figure 2B. It is evident that the denuder mode signal is higher than the light mode signal, indicating the evaporation of compounds (exact mass C_7H_9O) from the analyzed particles. However, the gas mode signal is nearly as high as the light mode signal, suggesting that this compound also exists in the gas phase. A compound like C_7H_9O, with a calculated volatility $\log(C^0) = 6.8$, is considered volatile, however other experiments also did detect benzaldehyde and benzoic acid in SOA [4, 8]. Additionally newest theoretical thermodynamic calculations of the interactions between benzaldehyde, benzoic acid, pyruvic acid and water – sulfuric acid clusters show the possibility of covering the clusters with layers of benzaldehyde and benzoic acid, where pyruvic acid is acting as a bridge for the volatile compounds [9].

In contrast, the monoterpene signal recorded at the mass of m/z = 154.159 ($C_{10}H_{16}$-NH_4^+) [9] shows no indication that monoterpenes would evaporate from the particle phase. The inlet thus allows differentiation between compounds present in the gas phase and others that partition also into the particle phase.

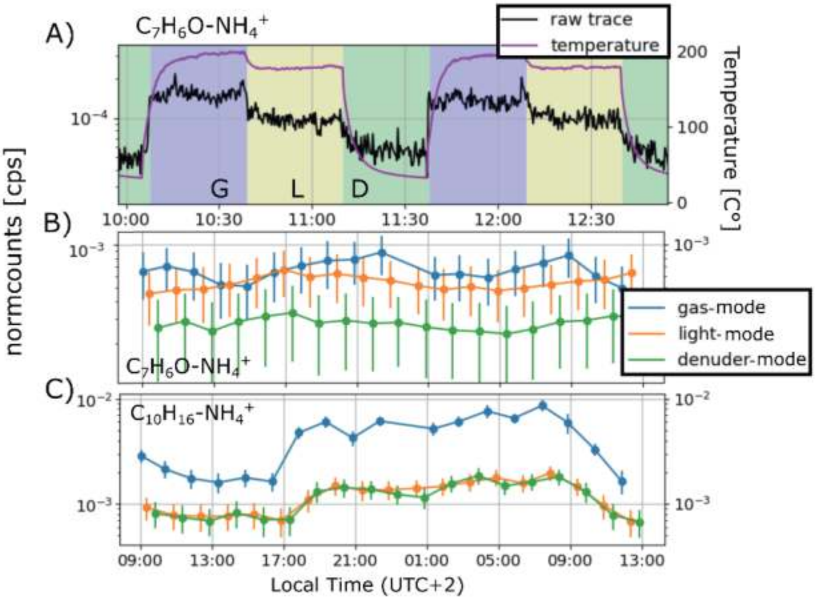

Figure 2: A) shows two measurement cycles of the raw C_7H_8O trace and the associated temperature in the cavity. Different modes are depicted in different background colors (blue = gas, yellow = light, green = denuder). B) depicts the diurnal variation of the mean signal in the different measurement modes. The lines are used to guide the eye. The particle- and gas- phase signal of C_7H_8O is compared to the signal of monoterpene compounds in F)

Discussion and Conclusion

From 1200 peaks recorded by the PTR3-TOF-MS in the outside air, 25 exact masses exhibited a significant signal of molecules evaporated by the infrared light. We tentatively assigned these peaks to aromatics, amines, organo-nitrates, furan derivatives, and methylglyoxal. Consequently, our results confirm the effectiveness of the new inlet in combination with the PTR3-TOF-MS for chemical analysis of OA, particularly for compounds with a low number of carbon atoms. However, one challenge that still remains is that lower volatile compounds tend to stick to the not heated inlet line, causing a long lasting decay of that ion signal when switching from light to denuder mode.

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Contributed Papers (Posters)

Characterization of volatile organic compound exchanges at a mixed forest site in the Belgian Ardennes

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Abstract

A good understanding of forest/atmosphere volatile organic compound exchange is crucial for emission, air quality and climate modelling. Dedicated campaigns in 2022 and 2023, spanning periods from mid-spring to late autumn, were set up at the Vielsalm ICOS mixed forest ecosystem station to enhance the knowledge on VOC sources and sinks below, within and above the canopy. Some preliminary results will be shown and the approach for further analysis will be discussed.

Introduction

Forests are the main global source of biogenic volatile organic compounds (BVOCs) which are precursors of ozone and other gaseous air pollutants and contribute to the formation and growth of secondary organic aerosol. As such BVOC emissions significantly affect the atmospheric oxidation capacity, air quality and climate. The emissions can be chemically diverse, are highly plant species-specific and strongly depend on meteorological, plant-physiological and phenological conditions. Even if emissions of the most emitted BVOCs, isoprene and monoterpenes, are generally well estimated by state-of-the-art emission models [1], uncertainties remain regarding the impact of ever more frequently occurring extreme weather conditions (e.g. long periods of drought or heat waves) as ecosystem-scale BVOC flux measurements in those conditions are still sparse [2]. Net half-hourly forest/atmosphere exchanges of oxygenated VOCs (OVOCs) are often bidirectional [3], depend on a multitude of processes taking place along the soil-canopy-atmosphere continuum, and are therefore less well understood in terms of driving parameters. Besides emissions by vegetation and other ecosystem components, such as soils and litter, physical processes (e.g. adsorption/desorption, dissolution in liquid films and re-evaporation), within-canopy chemical loss and formation and turbulent transport can all affect these (O)VOC fluxes. A good knowledge of those processes and their seasonality is important for improved BVOC emission, air quality and climate modelling [4].

To improve the knowledge on VOC exchanges along the soil-canopy-atmosphere and their seasonality, dedicated campaigns have been undertaken at a mixed forest site in the Belgian Ardennes from mid-spring to late autumn in 2022 and 2023. Specific questions to be answered from this campaign are:

> (1) Which (O)VOCs are exchanged above the mixed forest and in the trunk space, and how do fluxes relate to environmental, plant physiological and, if occurring, biotic or abiotic stress conditions?

(2) What is the contribution of the multiple sources and sinks along the soil-canopy-atmosphere gradient to the net above-canopy (O)VOC fluxes?
(3) What is the role of in-canopy chemistry on net ecosystem/atmosphere fluxes?

Experimental Methods

The measurements took place during 2022 (21 April - 27 October) and 2023 (20 April - 6 December) at the Vielsalm ICOS (Integrated Carbon Observation System) mixed forest ecosystem station in the Belgian Ardennes (50°18'18.2"N, 5°59'53.0"E, 450 m.a.s.l.). The vegetation at this site is a mixture of coniferous (mainly Douglas fir, Norway spruce and Silver fir) and deciduous (mainly European beech) species. The climate is temperate maritime, and the soil (50-100 cm deep) is classified as dystric cambisol. The station is equipped with a 52 m pylon to perform above-canopy eddy covariance (EC) flux measurements.

In 2022, ambient air was alternately sampled from the top of the tower, a location in the trunk space (3 m above the soil) and 5 additional vertical profile inlets along the tower, thus providing above-canopy VOC EC fluxes and VOC vertical concentration profiles. In 2023, the measurement sequence was extended with trunk space EC VOC fluxes. Care was taken to ensure an equilibrated partitioning of flux and vertical profile measurements in order not to bias average diurnal profiles over specific periods. The ambient air was pumped towards the log cabin through separate 60 m long, heated and thermally insulated 3/8" o.d. PFA tubes. Sonic anemometers, measuring the 3D wind speed, were located close to the tower top and trunk space air sampling points to enable eddy covariance flux calculations. Moreover, some additional sonic anemometers were added along the tower for improved turbulence characterization in the canopy space.

The measurement sequence was controlled by a manifold and the ambient air was subsampled by a PTR-TOF-4000 VOC analyzer (Ionicon Analytik GmbH). The PTR-TOF-MS instrument was operated at a drift tube pressure of 3.3 mbar. E/N was 135 Td and the inlet line and drift tube were kept at 80 °C. Mass spectra were acquired at 10 Hz and peak detection and peak system deconvolution were carried out using IDA software (on a daily basis).

Part of the ambient air flow from the top level was sent through a catalytic converter for regular background measurements (every 4.5 hours during half an hour), and calibration measurements were performed (every 3 to 4 days) by diluting a 19-Component VOC/N_2 mixture (Apel Riemer Environmental Inc.) in zero VOC air.

Fluxes were calculated from the high frequency VOC concentration and wind speed measurements by the custom python-based GEddySoft software, which is based on the matlab-based InnFlux open-source code [5].

Results and discussion

Processing of the 2022 data resulted in variable peak locations, obtained from the peak identification step, between independent IDA runs performed on a near-daily basis. The m/z peak locations were analyzed with the density-based spatial clustering in applications with noise (DBSCAN) algorithm to quantify the stability of m/z peaks identified with IDA. Considering only m/z peaks with stable location within instrument resolution (< HWHM), and fraction of data above the analyzer detection limits (> 50 %), 224 m/z values were considered for further analysis.

Significantly exchanged compound fluxes were found for 69 m/z ratios, based on the criterion that the |flux|>|LOD| during at least 3 of the 24 half-hours during daytime. Preliminary flux data of the 2023 campaign in this presentation are based on this selection of m/z data. Figure 1 shows the average diurnal variation of the 10 most exchanged compounds (in mass units) above the forest canopy from 20 April to 15 November.

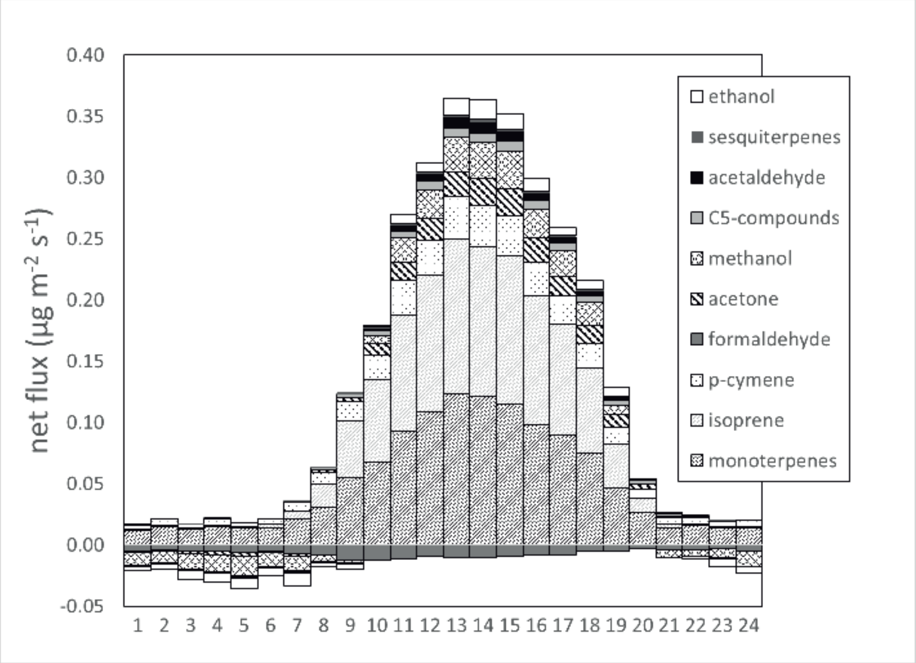

Fig.1: Average net fluxes diel evolution of the 10 most exchanged compounds during the entire 2023 campaign

Overall, emissions prevail but for some compounds such as methanol, formaldehyde and ethanol, depositions are equally important, especially during nighttime. Daytime MT emissions are equally high as isoprene emissions at this site, but MTs continue to be emitted during nighttime, in contrast to isoprene. Emissions at m/z 135.117 were tentatively identified as p-cymene, given a good correspondence between GC-MS and PTR-TOF-MS concentrations during the EMEP campaign in July 2022, and quantified using the H_3O^+/p-cymene rate constants and fragmentation pattern from the literature. Depositions dominated the exchanges at the end of the season and were also considerable at the start of the season (not shown). They, however, seldomly occurred during the dry and sunny period with high photochemical activity at the end of spring 2022, where the forest acted as a clear source of organic acids like formic acid and other oxidation products of biogenic compounds (e.g. MVK+MACR and nopinone), but also of highly reactive directly emitted species at higher m/z like sesquiterpenes (see Fig.2).

The temporal above-canopy flux variability over the 2 campaigns, together with a whole set of ancillary parameters available for the Vielsalm ICOS site will allow derivation of compound-specific emission capacities and information on the drivers of the exchanges. In combination with vertical VOC profiles, trunk space flux measurements and a 1D multi-layer canopy exchange model, the data are expected to give more insight into VOC sources and sinks along the soil-canopy-atmosphere continuum.

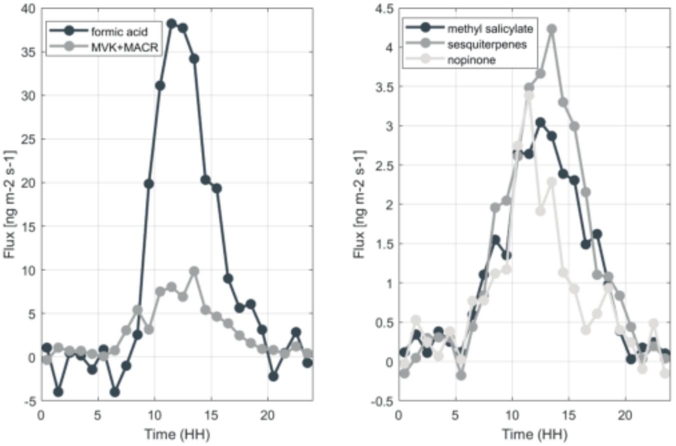

Fig. 2: average flux diurnal profiles of some important biogenic oxidation products and some directly emitted high m/z compounds during a dry and sunny period of high photochemical reactivity (1-20/06/2023)

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PTR-ToF-MS as an efficient sensor to drive new product formulations: volatilome characterisation of cricket flour enriched bread

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Abstract

This study aimed to exploit the advantages of PTR-ToF-MS as a sensor to support fermentation research and, in particular, to accelerate innovation in the bread industry. Due to the high demand for increased protein intake, especially in specific population targets, cricket flour was utilised as an alternative protein source to formulate a fortified bread. Different cereal flours (i.e. from soft and durum wheat and rye) and various management of the microbial resources as leavening agents (i.e. brewer's yeast, commercial sourdough preparation, and traditional sourdough from Trentino) were evaluated, also to assess the effects on the bread volatilome after cricket flour incorporation. PTR-ToF-MS proved to be a useful and rapid sensor and provides key information for the efficient design of new staple fermented food formulations enriched with alternative protein. The experimentation includes the use of resources of interest for Trentino-Alto Adige (Italy), underlining the importance of solutions also calibrated for the regional context.

Introduction

The search of new alternative proteins is a widely discussed topic due to the constant demand of new products which satisfy consumers expectation and take into consideration their environmental impact. One area of great interest is the use of edible insects as a food source for both animals and humans. Various studies have deemed edible insects to be a sustainable and cost-effective source of high-quality proteins for the diet [1]. However, this trend faces resistance from Western consumers who perceive them as unhealthy and unappetizing. Hence, while insect flours can be included in several formulations, the evaluation of sensory acceptability remains an open question. Many studies have described their flavor as tasty, buttery, herbal, or crunchy [2]; however, this can vary depending on the preparation methods. The technological objective of this research is to explore the diversity of cereal flours and microbial leavening agents on the volatilome of bread fortified with insect proteins. In order to speed up the innovation in the field, allowing rapid evaluation, the experimental plant proposed Proton-transfer-reaction, coupled with Time-of-Flight Mass Spectrometer (PTR-ToF-MS) as a green sensor with high sensitivity [3] for monitoring the volatile organic compounds (VOCs).

Experimental Methods

Doughs and bread preparation

18 types of dough, approximately weighting 200 g, were prepared, with different combinations of cereal flours, microbial resources and insect flour. Three different cereal flours were separately used for bread preparation: soft and durum wheat, and rye flours. Three different leavening agents were used: commercial sourdough preparation, a traditional sourdough from Trentino region, and brewer's yeast. Then, all the ingredients were added in the following amounts: 100 g of flour, 80 g of tap water, and 2,5 g of salt. As leavening agent was added 1 g of brewer's yeast or 20g traditional Trentino sourdough or 5g commercial sourdough. For each combination, a traditional test and one with the addition of insect flour were evaluated. The cricket-enriched doughs were prepared by substituting 15% of cereal flour with the insect one. After mixing all the ingredients, the doughs were left to ferment overnight. Each biological sample was independently replicated three times, resulting in a total of 54 samples.

PTR-ToF-MS analysis

After overnight fermentation and baking of bread, crust and crumb were powdered and homogenized. 3g of sample were put in 20 mL vials with PTFE/silicone septa for VOCs measurements by direct injection of the headspace mixture into a commercial PTR-ToF-MS 8000 apparatus (Ionicon Analytik GmbH, Innsbruck, Austria). Measurements were performed in an automated way by using a multipurpose GC automatic sampler (Autosampler, Gerstel GmbH, Mulheim am Ruhr, Germany) as described in [4]. All data detected and recorded by the PTR-ToF-MS were processed and analyzed using MATLAB R2017a (MathWorks Inc., Natick, MA, USA) and R (R Foundation for Statistical Computing, Vienna, Austria). Principal component analysis (PCA), analysis of variance, and Tukey's post-hoc test was performed to spot the differences in the volatile aroma compounds collected by the different breads.

Results and Discussion

Rapid screening of volatilome facilitated the evaluation of different management methods for bread preparation. The bread made with rye flour, which was also enriched with cricket flour, stood out from the other preparations. A consistent effect was observed in relation to the addition of insect flour in all preparations, resulting in a distinct difference from the corresponding regular bread. Additionally, the leavening agents played a crucial role in shaping the potential aromatic profile, with each one having its own specific VOCs profile, which was more similar for the bread trials made with soft and durum wheat flour. The findings suggest that the management of microbial resources significantly influences the aromatic content and therefore the distinctiveness of the bread, with potentialities to improve the sensory quality of insect flour-enriched bread. This is one of the first studies to report experimental evidence of the addition of alternative protein sources in breadmaking by evaluating different raw materials and different starter cultures in the same experimental plan.

Conclusion

The current research demonstrated the potential of PTR-ToF-MS, combined with tailored data analysis, to assess differences and similarities in volatile profile by distinguishing various preparation based on their chemical and physical characteristics. This preliminary investigation of volatilome effectively aided in quickly evaluating the varied management of yeast microorganisms in mitigating the impact of incorporating alternative protein sources. Overall, it proved invaluable in identifying the characteristics and parameters necessary for selecting the most suitable design for bread development.

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Fermentation, flavour, traditional products and cross-over solutions: the potential of PTR applications in the food and beverage sectors

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Abstract

Fermented foods and drinks represent a relevant resource for human nutrition and well-being. The use of microorganisms associated with traditional fermentations in new matrices represents a driver of innovation in the sector. Flavour analysis and volatile organic compounds determination represent a crucial area for characterisation and valorisation of traditional products and in driving innovation in fermented matrices. Here, we proposed an overview of the potential of PTR volatilomic studies in the food and beverage sectors, underlining the interest of the analytical technique in promoting traditional products characterisation and in developping cross-over solutions.

Introduction

Fermented products represent a dynamic sector, with a large component of traditional products and on the other characterised by continuous evolution, capable of offering solutions to improve the well-being and nutrition of different target populations. Fermentation also helps promote sustainable innovation and improve the quality of foods and drinks. There are thousands of traditional products, with a great diversity of microorganisms involved. Among the various dynamics of innovation in this sector, the relevance of the concept of cross-over fermentation in the development of new products should be highlighted. Cross-over fermentation has been defined by Dank *et al.* as "processes in which a microorganism from one traditional fermentation process is introduced onto a new substrate and/or to a new partner" [1]. The flavour and profiling of volatiles represent an element of continuity in the relationship between tradition and innovation in this sector, creating a driver for understanding the phenomena and valorising the resources.

Experimental Methods

The experimental methods followed foresaw the adoption of appropriate searching strategies in the scientific literature databases to perform a narrative review *i)* on the relevance of flavour and volatiles profiling in traditional products and in driving cross-over innovative solution of microbes from a traditional product into a new matrix/pattern and *ii)* on the potential of PTR-MS volatilomic analysis to support this kind of studies.

Results and Discussion

Flavour and volatile content are of huge interest in characterising fermented products and in designing innovative paths toward new product development. Volatile organic compounds (VOCs) represent molecules of high interest in studies on fermented products, being molecules produced by bacteria, yeasts and filamentous fungi, and, at the same time, they provide information on the qualitative state of the matrix [2-4] In consideration of this dual relevance, VOCs represent interesting markers for understanding the phenomena and promoting innovation in the sectors of traditional fermented products and new products. Proton transfer reaction mass spectrometry (PTR-MS) has demonstrated great versatility in terms of matrices and fermentation processes analysed [5], demonstrating potential applications not only in the evaluation of volatiles profiling of the diversity of traditional fermented products but also in the development of new products based on fermentation cross-over strategies. The narrative review also encompassed the recent outputs from ongoing research activities supported by the projects ‘iNEST’, ‘ONFOODS’ and ‘AGRITECH’ [Italian National Recovery and Resilience Plan (NRRP) projects financed by the European Commission’s Next Generation EU programme].

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Volatile organic compounds and new particle formation from agricultural recycling of organic waste products

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Abstract

Secondary organic aerosols (SOA) are one of the main uncertainty sources in the current understanding of the Earth's Climate. It is known that agriculture contributes to primary aerosols emissions but there is no estimate for the secondary organic aerosol formation from precursor gas phase. Organic waste products are applied to cropland as fertilizers and in this work we show that they are an unaccounted source of nucleation precursors (e.g. skatole, C_9H_9N). The skatole emission and nucleation rates due to ozone reactivity were determined in the laboratory and based on our results, SO_2 plays a key role in the oxidation of skatole and leads to new particle formation. The results presented here provide new insights into this novel nucleation mechanism and aid our understanding of the organic waste agricultural recycling contribution to the aerosol balance in the atmosphere.

Introduction

Atmospheric aerosols constitute a major concern for human health and impact Earth's radiative balance both directly and indirectly, through their influence on cloud properties. Atmospheric aerosols act as cloud condensation nuclei, thus altering cloud albedo, structure, and lifetime. They also represent a major health and economic issue since the particulate pollution is responsible for approximately 3 million premature deaths per year and projected to increase to 6 million in 2050 [1]. Volatile organic compounds (VOC), emitted into the atmosphere from anthropogenic and biogenic sources, are major players in atmospheric photochemical reactions that contribute to ozone formation. VOCs are also responsible for secondary organic aerosol (SOA) formation in the presence of photo-oxidants [2].

The recycling of different types of organic waste products (OWP) from livestock, urban or industrial sources is currently being promoted as a substitute for mineral fertilizers for agricultural land. The OWP recycling in agriculture can increase the organic matter stocks in soil and thereby improve soil chemical fertility, stimulate microbial activity or increase water retention[4]. It also improves the recycling of nutrients and can decrease the use of mineral fertilizers, which are non-renewable resources. However, the application of OWP to agricultural soils can present different health and environmental risks: some contaminants can accumulate in the soil, degrade water quality or be emitted into the atmosphere [3-6]. A recent study [7] showed that compared with boreal forests, agricultural land areas are 10–20 times more efficient in producing growing aerosol particles and probably several times more efficient in eventually producing new cloud condensation nuclei. Globally, agriculture occupies more than 37% of Earth's land area while forests contribute to 30.7%. A 15 times higher contribution to new particle formation of agricultural land, compared to boreal forests has been observed and is yet unaccounted for in global models [7].

The study presented here aims at providing new insights into processes involved in the formation of SOA from organic waste products as a result of the reactivity of VOCs emitted by these amendments with ozone.

Experimental Methods

Organic waste products samples were introduced into a Teflon coated reaction chamber (0.03 m^3, 0.2 m height, 0.27 m width, 0.55 m length) and exposed to ambient levels of ozone. A high-resolution proton transfer reaction time-of-flight mass spectrometer (HR-Qi-PTR-TOF-MS, Ionicon Analytik GmbH) was used for the VOC concentration (drift tube 4 mbar, inlet temperature 80 °C and the drift voltage 1000 V, extraction voltage 44 V and E/N 132 Td). The ozone, NOx and NH_3, SO_2, CO_2 and H_2O were continuously measured. VOCs were also trapped on Tenax TA cartridges for Thermal Desorption – Gas Chromatography – Mass Spectrometry analysis. Tubes were desorbed using a thermo-desorption unit. VOCs separation was carried out using an Agilent 7890B gas chromatograph on a capillary column. A scanning mobility particle sizer (SMPS 3938; TSI) was used for the particle number concentration and size distribution measurements.

Results

Figure 1 shows a typical example of a sewage sludge experiment. Upon the sample introduction into the chamber, a strong burst release of methylindole (m/z 132.087 $C_9H_9NH^+$) was observed. Following the initial burst, sewage VOC signals stabilized. A production of NH_3 and SO_2 was also observed. NOx mixing ratios were low (2-3 ppb) during the experiments. Within a few seconds of the initial exposure of sewage sludge samples to O_3 in the chamber, the signal of m/z 132.087 $C_9H_9NH^+$ decreased and gas-phase oxygenated and nitrogen containing molecules increased, in particular m/z 136.075 $C_8H_9NOH^+$ and m/z 164.070 $C_9H_9NO_2H^+$ (Figure 1c). The O_3 was continuously monitored into the chamber and remained at around 55 ppbv at the entrance of the chamber. Particles appeared almost instantaneously after O_3 injection. The particle number and size distributions (Figure 1a) span the entire measured size range from 2 to 64 nm electrical mobility diameters, therefore showcasing newly formed particles. During these experiments, the particle number concentration reached a maximum of 10^6 particles cm^{-3} within less than 2 min. This lead to a particle nucleation rate up to 1.1 10^6 cm^{-3} s^{-1}.

A comparison of the VOC data measured with three independent techniques (proton-transfer reaction mass spectrometry; gas chromatography coupled to mass spectrometry and ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry) was performed to identify the detected ions. The m/z 132.08 $C_9H_9NH^+$ was identified as skatole. As shown in Figure 1 c, two oxygenated products were observed in the gas phase (m/z 136.075 $C_8H_9NOH^+$ and m/z 164.070 $C_9H_9NO_2H^+$) subsequent to ozonolysis reactions. These oxidation products contain the carbon skeleton of their precursor skatole. Gas chromatography analysis performed before and after ozonolysis and liquid chromatography performed on collected particles revealed that m/z 164.070 $C_9H_9NO_2H^+$ corresponds to 2-acetyl phenyl formamide. The reaction of ozone with skatole proceeds by the Criegee mechanism by an initial O_3 addition to the double bound to yield a primary ozonide which decomposes into two stabilized Criegee intermediates [8].

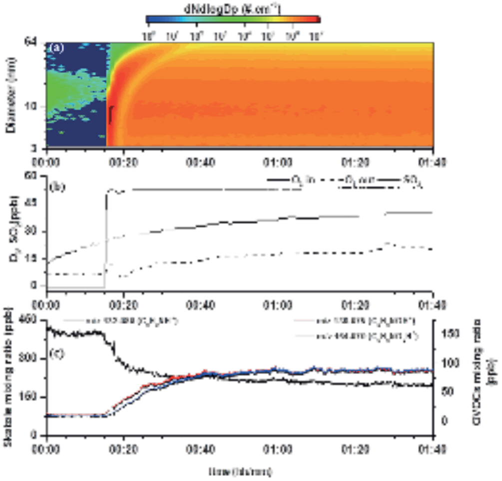

Figure 1. Typical sewage sludge ozonolysis experiment. (a) Temporal evolution of particle number concentration and size distribution. (b) Temporal evolution of O_3 entering the chamber (black line), O_3 measured at the exit of the chamber (black dotted line, O_3 out) and SO_2 (grey line). (c) Temporal evolution of m/z 132.080 $C_9H_9NH^+$ (black line, left axis), m/z 136.075 $C_8H_9NOH^+$ (red line, right axis) and m/z 164.070 $C_9H_9NO_2H^+$ (blue line, right axis).

Discussion

This study gives new insights into the gaseous emissions and aerosol formation from organic waste products. It has been shown that the agriculture contributes to about 16% of the PM2.5 primary emissions and to ~18% of the PM10 emissions [9]. However, there is no estimate for the SOA formation from precursor gases emitted by agriculture. Recent studies show that aerosol formation in regions of intensive ammonia emission may have been underestimated. A large part of the gap between modeled and measured aerosol concentrations might be explained by these underestimated agricultural sources. Moreover, agricultural particles were thought to be generated during the specific operations and processes or secondary formed due to NH3 emissions. In this study, a new particle formation mechanism from agriculture that does not involve ammonia is highlighted [4].

This study shows that indoles, and more specifically skatole, together with SO2 emitted by sewage sludge, are the species pertinent to initiate reactions with atmospheric relevant ozone mixing ratios leading to particle nucleation and growth. The indole compounds are present at field scale during spreading on agricultural surfaces. For example, skatole production and release of 4.91 - 8.3 µg m-2 min-1 following land spreading of pig slurry [10] or land application of swine manure slurry [11] have been shown. Our emissions are estimated at around 50 µg m-2 min-1 of skatole. Various reaction products were observed in the gas and particulate phases. Among them, 2-acetylphenyl formamide was identified as the main skatole ozonolysis product and formation pathways were proposed. Furthermore, the chemical analysis of particles shows that organic compounds contribute to growth in this size range. All these statements are supported by chamber measurements using commercially available skatole. The high reactivity of skatole towards ozone results in considerable enhancement of condensable reaction products that might partition into the aerosol phase and potentially act as cloud condensation nuclei [2].

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Breath metabolomics as a potential tool for the therapeutic drug monitoring of CFTR modulators in adults with cystic fibrosis.

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Background

The combination of ivacaftor/tezacaftor/elexacaftor, a set of cystic fibrosis transmembrane conductance regulator (CFTR) modulators, has been shown to restore CFTR activity in individuals with the p.Phe508del mutation, potentially leading to improved respiratory function and quality of life. Our hypothesis posited that this treatment induces profound metabolic changes in the lungs, resulting in significant alterations in the volatilomic profile of exhaled breath. The primary objective of our study was to evaluate the interest of breath analysis in monitoring the short-term response to the triple combination.

Methods

A prospective open-label study was conducted at Foch Hospital, involving ten adult patients initiating triple therapy (NCT05295524). Proton transfer reaction mass spectrometry was used to analyse exhaled breath before treatment, during the first week, and after one month. Data analysis employed the ptairMS package [1] with machine learning tools. Clinical symptoms, lung function, and sweat tests were assessed at each visit.

Results

Among 168 consistently detected volatilomic features, six compounds exhibited significant decreases (p-value F-test mixed model < 0.05) in all patients during the first week of treatment. VOC concentrations changes were correlated with clinical and biological outcomes such as FEV1 and sweat chlorides.

Conclusions

The triple therapy with CFTR modulators influences the composition of exhaled breath, with detectable modifications observed within the initial days of treatment. Ongoing investigations are focused on annotating and identifying the origin of these compounds. Breath metabolomics might become a tool for therapeutic drug monitoring in cystic fibrosis.

Acknowledgments:

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VOC flux measurement in China's megacity by PTR-TOF-MS

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Abstract

We conducted urban volatile organic compound (VOC) flux measurements in Beijing, a megacity in China, using the eddy covariance (EC) technique with a Proton transfer reaction quadrupole ion guide time of flight-mass spectrometer (PTR-QiTOF-MS) during the summer of 2021.

Introduction

Volatile Organic Compounds (VOCs) in the atmosphere are known to be precursors to both particulate matter and ozone [1]. However, accurately quantifying VOC emissions in urban regions still poses a significant challenge, resulting in significant uncertainty regarding the levels and sources of anthropogenic VOC emissions [2-4]. Recent developments in proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS) and eddy covariance techniques have facilitated the direct quantification of volatile organic compound (VOC) emissions in urban regions [5].

To directly quantify the VOC emissions and investigate the profile of emission sources in typical urban regions of China, we conducted VOC flux measurement in a megacity in Beijing, China.

Experimental Methods

VOC flux measurement was conducted at the 325-meter meteorology tower (39°58′N, 116°22′E) in the Institute of Atmospheric Physics, Chinese Academy of Sciences. Located between the North 4th Ring Road and North 3rd Ring Road, ~300 meters away from the Beijing-Tibet expressway, this tower has witnessed fast urbanization in the past 40 years. The flux sample inlet was placed at the 102-meter platform to ensure the measurement height was below the planetary boundary layer height and well above the roughness sublayer.

10 Hz wind speed and direction data were collected by the IRGASON system that integrates a CO_2/H_2O open-path gas analyzer and 3D sonic anemometer (Campbell Scientific, INC., USA). This system is mounted at the southeast cantilever at the 102-meter platform, 2 meters away from the tower structure. A specially designed L-shaped metal support was applied that can hold the anemometer parallel to the cantilever but with a 45-degree rotation. The flux sampling inlet was mounted at the same cantilever but 40 cm away from the center of the CO_2/H_2O infrared path. The air sample was delivered down to the ground to be analyzed using a high-volume GAST vacuum pump (Model: SG608X) through ~150-meter Teflon tubing with ½ inch OD. The flow rate was ~45 LPM, leading to ~13 seconds of traveling time through the tubing.

VOC concentrations were measured by a PTR-QiTOF-MS with hydronium ion chemistry. Detailed setup of the drift tube pressure, E/N, etc. can be seen in preview papers [6, 7]. Due to the pressure drop in the tubing close to the ground, the sampling model of the PTR- QiTOF-MS has been modified with a greater ID of the capillary tubing.

Results

We calculated mixing ratios for 766 NMVOC ions (exceeding detection limit) and screened out 199 NMVOC species with detectable flux. Figure. 1 presents the time series and the diurnal patterns of the measured NMVOC flux in our observation. ~63% of data points passed the quality control criteria outlined in the method were included in the quantitative analysis. Our measurement reveals significant daytime emissions of NMVOCs, with minor emissions occurring during nighttime, which reflects the profiles of human activities and biogenic sources in China's cities.

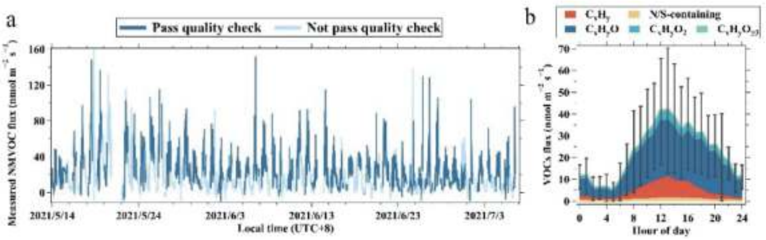

Figure. 1. (a) Time series and (b) diurnal pattern of NMVOC flux in Beijing. The NMVOC flux data is filtered by the level of quality class.

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Using a PTR-TOF 6000X2 with EVR and CHARON at the AURA atmospheric simulation chamber

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Abstract

In the late summer 2023 we received our PTR-TOF 6000X2 with EVR, CHARON and SRI options for use with the Aarhus University Research on Aerosol (AURA) atmospheric simulation chamber [1]. We will present the setup and preliminary results from dark ozonolysis of the monoterpene sabinene, as well as preliminary results related to oxidation of marine VOCs in the AURA chamber.

The core of the AURA chamber is a 5 m^3 cuboid FEP Teflon bag which can be temperature controlled in the range -16 °C to 26 °C. Water vapor can be injected into the AURA chamber such that a range of 0-100 % relative humidity can be covered. The PTR-MS has been installed outside the cold room and the VOC inlet is connected to the Teflon bag by a 2 m long 1/16” SilcoNert treated stainless-steel tube inside a custom built two zoned heated hose. The CHARON is sampling from the Teflon bag through a combination of stainless-steel tubing and conductive PFA tubing.

The gas to particle partitioning of organic compounds [2] is to be investigated using the CHARON PTR-MS. We have observed expected oxidation products (e.g. sabinalic acid/norsabinonic acid) in both gas phase and particle phase from dark ozonolysis of sabinene. Sources of marine VOCs for experiments in AURA are currently being explored. Preliminary results from these studies will be presented.

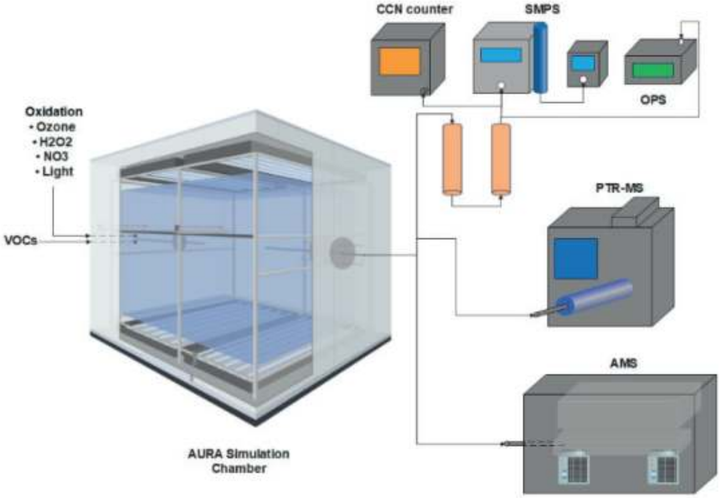

Figure 1: Schematic of the AURA atmospheric simulation chamber including a selection of the measurement instruments.

Acknowledgements

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Biogenic volatile responses of arctic tundra to warming and elevated atmospheric CO_2: lab-based mesocosm studies

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Abstract

Volatile Organic Compounds (VOCs) play a critical role in the physical and chemical properties of the atmosphere and in regulating Earth's climate. They primarily originate from biogenic sources and often exhibit strong temperature dependencies, making them extremely sensitive to temperature changes. In addition, increasing ambient CO_2 concentration has been shown to decrease isoprene production by plants, but it also may promote the biomass growth of vegetation. However, the projection of potential changes in Arctic biogenic VOC emissions in response to the combined effect of temperature and CO_2 concentration remains largely unexplored. Here, we collected mesocosms representative of the Arctic tundra during the late growing season in August, and incubated them under different projected climatic conditions. During the incubation, they were placed in polycarbonate growth chambers for the measurement of VOC emission rates using a dynamic flow-through method. VOC emissions were measured in real-time by a PTR-ToF-MS and also through adsorbent tubes, which were later analyzed by a GC-MS to assist in compound identification. The findings from this study will enhance our understanding of how VOC emissions in the Arctic tundra will respond to a future climate characterized by warmer temperatures, higher CO_2 levels and other associated climatic factors.

Introduction

Volatile Organic Compounds (VOCs) are critical players in influencing both the physical and chemical properties of the atmosphere and playing a pivotal role in Earth's climate regulation. As highly reactive gaseous carbon compounds, VOCs have multiple climatic consequences when released into the atmosphere. They are susceptible to oxidation by atmospheric hydroxyl radicals (•OH), a process that competes with the atmospheric oxidation of methane, thereby extending the lifetime and global warming potential of methane [1]. Additionally, the photochemical reactions between VOCs and NOx can produce hazardous tropospheric ozone. Furthermore, VOCs contribute to aerosol formation and the growth of cloud condensation nuclei, which scatter sunlight and affect Earth's radiation balance [2].

In the Arctic, VOCs predominantly originate from biogenic sources and their emission is strongly temperature dependent. This is particularly crucial in the Arctic region, currently undergoing rapid global warming at a rate twice the global average [3]. Arctic and alpine areas have witnessed a surface air temperature increase of 0.3 K per decade over the past three decades, with predicted temperature increases expected to be double that of the global rate.

However, the potential changes in Arctic biogenic VOC emissions in response to the combined effects of temperature and CO_2 concentration remain largely unexplored. Our objective is to refine the current estimations of VOC emissions from tundra ecosystems in the context of future climate conditions. To this end, we incubated representative mesocosms of the Arctic tundra and conducted a factorial experiment that incorporated variations in temperature and ambient CO_2 concentrations. This approach was designed to investigate the potential responses of the Arctic tundra to future climatic changes, particularly concerning biogenic VOC emissions.

Experimental Methods

Mecososm collection and incubation

The mesocosms, representative of the Arctic tundra, were collected in the vicinity of Abisko National Park (68°25'N, 18°15'E), Sweden, during the peak of the growing season in August. The dominant plant species in these samples was *Empetrum nigrum*, underlain by a layer of moss mats. Following collection, the mesocosms were transported to Copenhagen for incubation in a climate-controlled chamber, which simulated the seasonal transitions of autumn, winter, and spring, allowing the plants to go through a cycle of dormancy and revival.

Post-rejuvenation, the mesocosms were divided into three temperature treatment groups. Throughout the incubation period, the mesocosms were periodically moved to a specialized measurement chamber to conduct the VOC flux measurements.

VOC measurements

During the measurement process, the mesocosms were placed in polycarbonate chambers and flushed with activated charcoal-filtered ambient air. The outflow air was then directed to a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS 1000 ultra, Ionicon Analytik) for real-time analysis of VOC concentrations. Additionally, a portion of the outflow air was diverted through adsorbent cartridges (hydrophobic 150 mg Tenax TA/200 mg Carbograph 1TD, Markes) to capture the VOCs. These captured compounds were later thermally desorbed and analyzed by a gas chromatography-mass spectrometry to aid in compound identification.

After ~30 min measurement at ambient CO_2 concentration, additional CO_2 was introduced into the inflow air at a controlled rate to elevate the ambient CO_2 level to 800 ppm. The instantaneous VOC response of the plants to this increased CO_2 concentration was recorded using the PTR-ToF-MS and the adsorbent cartridges, as previously described. Subsequently, light and soil moisture conditions were also modified to assess their impact on VOC emissions from the Arctic tundra. Later, the mesocosms were incubated in an environment with elevated CO_2 levels (~800ppm) for approximately three weeks. Following this period, their VOC emissions were measured again as described above.

Following the completion of all experiments, the plants were harvested, dried, and separated into segments such as leaves, branches, and roots. The weight of each segment was then measured. Additionally, the weight of the moss layer was also recorded.

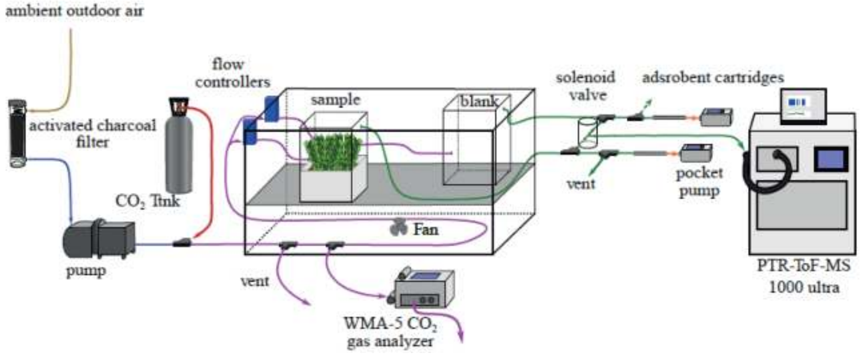

Figure 1: experimental setup of the tundra mesocosm incubation and VOC analysis.

Results and Discussion

Data from the experiment is currently under processing. Preliminary data showed strong temperature and light responses of most VOCs, as well as consistent suppression of isoprene emissions under elevated CO_2 levels. We expect to show how Arctic tundra vegetation VOC emissions respond to elevated CO_2 concentration and how the response interacts with temperature and other environmental factors. The results will improve our future predictions of VOC emissions from tundra ecosystems, and increase our understanding of their atmospheric and climatic feedbacks and implications associated with this ecosystem in the future.

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BVOCs in forest and agricultural environments

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Abstract

Biogenic (BVOCs) and anthropogenic (AVOCs) volatile organic compounds were measured in the Czech Republic at the forest (Bílý Kříž) and agricultural (Košetice) sites by PTR-TOF-MS 6000 X2 in summer of 2022 and 2023. Here we present preliminary results from Košetice site focusing on diurnal courses of monoterpenes, isoprene, and 2-methyl-3-buten-2-ol (232MBO). The results show that the hot summer period (3.-16. July 2023) is associated with high monoterpene concentrations at night due to boundary layer shrinking. Similarly, the highest concentrations of isoprene and 232MBO are overnight. In contrast, concentrations of other BVOCs (e.g., monoterpenes, isoprene) peak during the central hours of a day suggesting that their emissions are likely sunlight-driven. To identify the pollution associated with the research infrastructure operation, the ratio between toluene and benzene concentrations was investigated too. At the poster, BVOCs and AVOCs from Bílý Kříž will be present too.

Introduction and Experimental Methods

Although being present in low concentrations, BVOCs and AVOCs play pivotal roles in atmospheric chemistry due to their fast reactivity and potential for tropospheric ozone formation. Therefore, it is worth investigating their diurnal concentration profiles, especially during hot summer months and in different field environments. Here we report selected measurements of BVOC and AVOC concentrations in a mountainous coniferous forest and a typical highland agricultural site with intensive management practices. Stations are equipped with plethora of meteorological instrumentation, which allows to investigate possible correlations to VOCs.

Experimental sites

Bílý Kříž (900 m a.s.l., NE of the CZE) is covered by mountainous Norway spruce forest. It forms part of ICOS-ERIC (Integrated Carbon Observation System) and AnaEE-ERIC (Analysis and Experimentation on Ecosystems). This area has a moderately cool (mean air temperature 6.6◦C) and humid (mean humidity 84.7%) climate with a high annual precipitation (year sum is 1152 mm).

Košetice (close to Křešín u Pacova, 530 m a.s.l., middle of CZE) is an agricultural site coved by arable land with patches of forests. It consists of an atmospheric tower (250 m tall) and a smaller agricultural tower. It forms a part of European infrastructure networks ICOS, GMOS (Global Mercury Observation System), and ACTRIS (The Aerosol, Clouds and Trace Gases Research Infrastructure). In 2023 winter barley was grown in the vicinity of the station. This area has a moderate temperature (annual mean air temperature 8.6◦C) and humid (annual mean relative air humidity 77.2%) climate with medium annual precipitation pattern (total annual mean is 665 mm).

PTR-TOF measurements and data analysis

The PTR-TOF-MS 6000 X2 (Ionicon, Innsbruck, Austria) was deployed at Bílý Kříž in the summer of 2022 and at Košetice tall tower in the summer of 2023. The aim was to measure the diurnal courses of BVOCs and AVOCs. The instrument was operated in H_3O^+ mode, zero and calibration was performed every day from a zero-air generator and calibration gas cylinder (ApelRiemer, FL, USA). The frequency of measurement was 10Hz at Bílý Kříž and 1s at Košetice. The inlet line was connected to longer PTFE lines with flow driven by a pump. Air was sampled 2m above forest at Bílý Kříž (20m above ground) and 4m above ground at Košetice. At Bílý Kříž eddy covariance fluxes were measured too. Data post-processing was performed by IDA software (Ionicon, Innsbruck, Austria) with subsequent MatLab (MathWorks, MA, USA) script analyses. High-frequency concentration data were averaged to reach 30-min periods.

All the VOCs present were calculated with regard to their isotopic composition presented in nature. 232MBO was calculated from its fragment at m/z 87.0804, assuming that 232MBO fragments with the rate of 25% into the parent ion (Karl et al., 2012).

Results and Discussion

BVOCs are dominated by monoterpenes recorded at m/z 137.1325, followed by isoprene at m/z 69.0699. 232MBO concentration was calculated from its fragment, showing a similar diurnal profile as isoprene. However, no sesquiterpenes were detected, likely due to their very short lifetime. Another reason could be, that barley plants were already in the final ripening stage, emitting thus lower amounts of BVOCs into the atmosphere. The diurnal course of selected BVOCs is depicted in Figure 1.

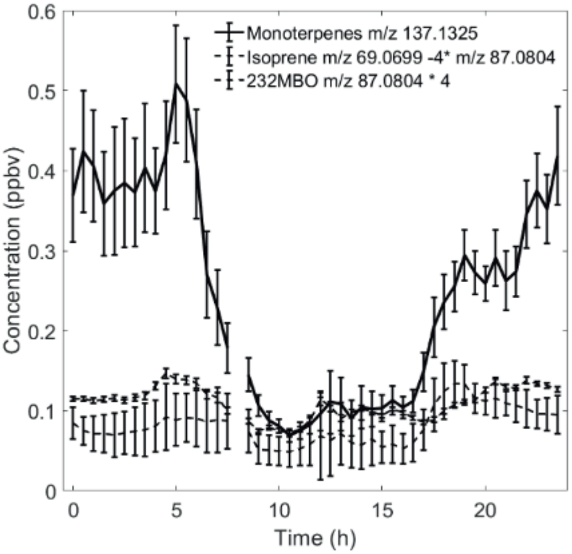

Figure 1: Diurnal courses of total monoterpenes, isoprene and 232MBO (BVOCs) at the agricultural site Košetice expressed as an average for the period of 3-16. July 2023. Overbars represent the standard error of the mean.

In order to track the origin of toluene and benzene pollution, AVOCs were investigated as toluene to benzene ratio. Typically, the ratio is high (> 1.5) at heavily polluted sites, whereas it is close to unity at background locations. Here, the overnight ratio is very high (night maximum 1.6), suggesting fresh AVOC emissions very close to the sampling point (see Figure 2). The diesel engine of the atmospheric tower elevator was identified as the likely source of emissions. On the contrary, the ratio decreases to unity during the day as remote vehicle transport emissions contribute are dominant source of AVOCs.

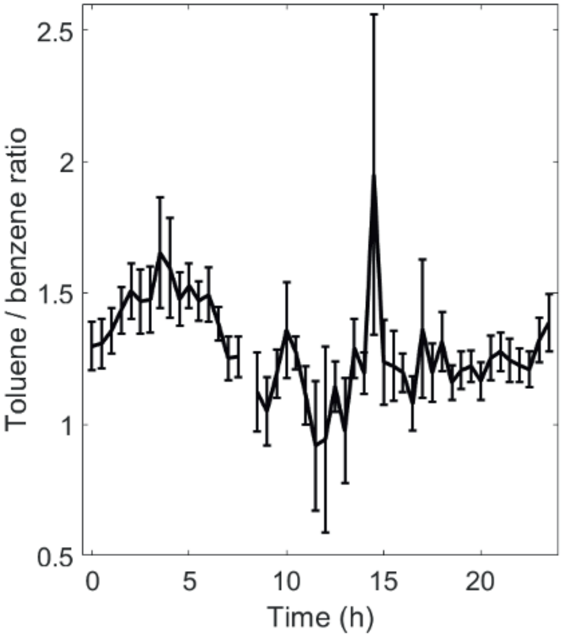

Figure 2: Diurnal course of toluene to benzene concentration (ppbv / ppbv) ratio as an average from 3-16. July 2023, Košetice. Overbars represent the standard error of the mean.

Acknowledgements

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Characterization of kefir-like cereal-based beverages volatilome during fermentation by using PTR-Tof-MS

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Abstract

This work aimed to characterize the volatile profile of new dairy-like plant-based fermented beverages using cereal as fermentable substrates. Barley, corn, and oat flours underwent fermentations, which were carried out by separately inoculating milk kefir and water kefir grains. Milk was included among the matrices in the study to compare the results with a standard kefir production. Each experimental mode was also evaluated with or without the addition of a *Lactoplantibacillus plantarum* strain selected for the *in situ* production of riboflavin in the food matrix. PTR-ToF-MS allowed the real-time, direct, and non-invasive monitoring of microorganisms' volatiles and food volatilomics during the fermentation of products.

Introduction

Functional beverages stand out as a rapidly expanding segment within the realm of emerging food categories. Milk kefir, an ancient fermented beverage, holds a place within the domain of functional foods, acknowledged for its established health-enhancing properties. Milk kefir is commonly produced using a combination of lactic acid and alcoholic fermentation by microbial flora, conferring a small amount of ethanol content and a unique characteristic flavour to this product. The traditional method of making milk kefir draws in kefir grains that are mixed cultures consisting of various yeasts, lactic acid bacteria and acetic acid bacteria that co-exist in a symbiotic association and are responsible for an acidealcoholic fermentation [1]. Similarly, water kefir is prepared with a sucrose solution with or without fruit extracts fermented by kefir grains [2].

Different formulations and biotechnological innovations were recently proposed to develop kefir-like products with improved sensory, nutritional, and functional features [3]. For instance, kefir grains were used to ferment non-dairy raw materials, such as vegetables and cereals to produce functional beverages enriched in vitamins, bioactive compounds or able to vehicle potential health-promoting bacteria [4, 5].

In this contest, volatile organic compounds (VOCs) serve as valuable indicators to monitor bioprocesses, offer insight into the quality of the matrices and can be considered as promising biomarkers in terms of sensory properties. Proton-transfer-reaction, coupled with Time-of-Flight Mass Spectrometer (PTR-ToF-MS), represents a green, rapid and non-invasive analytical solution to screen microbial volatilome and was widely applied in the field of fermentation monitoring [6].

This work aimed to evaluate the dynamic changes of volatile profile of kefir-like beverages during the fermentation of cereal matrices by PTR-ToF-MS coupled with a multipurpose GC automatic sampler.

Experimental Methods

Cereal-based fermentable products were obtained from oat, corn and barley flours, according to the method previously reported by Yépez et al. [3]. Milk was included in the study as a control of standard kefir production. Fermentations were carried out using two commercial kefir starters: i) water kefir preparation and ii) milk kefir preparation with or without the addition of *Lactoplantibacillus plantarum* strain.

Volatile organic compounds (VOCs) produced during fermentation were sampled automatically every 2 hours for 48 hours at 25°C by dynamic headspace module of multipurpose GC automatic sampler (Gerstel GmbH, Mulheim am Ruhr, Germany) into a PTR-ToF-MS 8000 device (Ionicon Analytik GmbH, Innsbruck, Austria). All PTR-ToF-MS data collected were processed and analyzed using MATLAB R2017a (MathWorks Inc., Natick, MA, USA) and R (R Foundation for Statistical Computing, Vienna, Austria).

Results and discussion

The differences in the matrix formulation, starter and additional inoculation within the kefir beverage types under investigation affected their VOCs profiling in all samples.
A general evolution in the time of milk and kefir-like associated volatilomes has been observed, with a strong influence of the volatilome profile in the case of barley by the active microorganisms, as observed by Yépez et al. [3]. The formation of volatile higher alcohols and corresponding esters during kefir fermentation was influenced by the composition of the starter and inoculation with *Lactoplantibacillus plantarum*. Considering different matrices, the inoculation has an influence on the VOCs profiling of corn and oat kefir than that of barley and milk beverages.
The differences among kefir beverage types observed in terms of VOCs profile are expected to produce different sensory properties, particularly regarding the consumers overall liking.

Conclusion

The evidence gathered in the present study pointed out that PTR-ToF-MS measurements permitted the assessment and monitoring of VOCs during the fermentation processes to track their evolution and kinetics. Acquired results thus provide information on possible consumer sensory product quality. Moreover, taking into account the increasing complexity of the consumers' needs and rapid changes of food market, the integrated technological approach proposed in this study is useful for the development of innovated fermented products. This outcome suggests that further research is required to steer technological interventions to maximize the efficiency of plant-based fermented beverage design.

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Characterization of hazelnut volatilome evolution during roasting by PTR-ToF-MS, GC-IMS, GC-MS and advanced data mining methods

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Abstract

This study focuses on the comprehensive characterization of the volatilome of hazelnuts, particularly during the roasting process, using a combination of rapid and conventional analytical techniques. The hazelnuts, sourced from different geographical origins, underwent roasting, and the resulting paste samples were analyzed for volatile organic compound (VOC) profiles. The analytical methods employed include PTR-ToF-MS, GC-IMS, and GC-MS. The study highlights the effectiveness of a combined analytical approach for volatilome characterization and the use of rapid tools with automated data processing.

Introduction

Hazelnuts (*Corylus avellana L.*) hold considerable industrial importance, especially in the confectionery sector. Almost the entire industrial utilization of hazelnuts involves processed products derived from roasted kernels, such as hazelnut paste [1]. The roasting step plays a crucial role in the industrial processing of hazelnuts, significantly altering the composition of the volatile fraction and, therefore, the resulting aromatic profile [2]. Furthermore, despite Turkey being the main producing country, the industrial hazelnut supply chain includes numerous cultivars and blends from various geographical origins. Within this context, it is crucial to identify characteristic patterns in the formation/release of volatile organic compounds (VOCs), and to investigate distinctions among cultivars concerning the thermal treatment and its impact on the volatilome.

In this study the evolution of hazelnut volatilome was investigated analyzing hazelnut paste samples with increasing degree of roasting, by applying in parallel rapid (PTR-ToF-MS and GC-IMS) and conventional (GC-MS) analytical techniques.

Gas Chromatography coupled with Mass Spectrometry (GC-MS) is the standard technique for VOC characterization, albeit involving a time-consuming pre-concentration step and relatively long analysis time. In contrast, direct injection mass spectrometry (DIMS) techniques like Proton Transfer Reaction Mass Spectrometry (PTR-MS) offer sensitivity and high throughput, proving particularly beneficial for large samplings in quality control and phenotyping. However, in complex matrices like roasted hazelnuts, annotation is challenging due to the presence of isomers, fragments, and clusters. Combining DIMS with simultaneous GC-MS analysis on selected samples helps address these challenges and provides more comprehensive results [3]. The second rapid analytical technique employed is Gas Chromatography coupled with Ion Mobility Spectrometry (GC-IMS), gaining popularity in food volatilomics for untargeted fingerprinting approaches [4]. Its instrumental ease-of-use and relatively short analysis time per sample contribute to its appeal. While predominantly positioned as a method for untargeted fingerprinting, the prevalent approach for GC-IMS peak detection often relies on manual selection. This process is time-consuming and susceptible to the operator's subjective judgment, and the development of automated workflows for GC-IMS data processing is a research subject of increasing interest.

This study aims to: i) characterize the volatilome of hazelnuts, studying its changes during roasting and differences among three industrially employed cultivars; ii) develop an automated untargeted peak detection workflow for GC-IMS data; and iii) perform a comparative analysis of PTR-MS, GC-IMS, and GC-MS when applied simultaneously to the identical sample set, critically evaluating the potential of a comprehensive analytical strategy integrating these methods.

Experimental Methods

Samples

This study utilized hazelnuts sourced from three different geographical and botanical origins: "Tonda Gentile Romana" monocultivar hazelnuts from the Lazio region (Italy), "Tonda Gentile delle Langhe" monocultivar hazelnuts from the Piemonte region (Italy), and "Akçakoca" hazelnuts from Turkey. The roasting process was conducted using a pilot-scale infrared roaster. Regular collections of small kernel aliquots (150-200 g) were made throughout the thermal treatment to obtain samples at varying roasting intensities. Each aliquot was processed to yield paste samples, and their volatile organic compound (VOC) profiles were characterized using three different techniques.

Analytical platforms

VOC measurements were conducted using three analytical methods: SHS-PTR-ToF-MS (PTR-ToF-MS 8000, Ionicon, Austria, equipped with an MPS Multipurpose Sampler, GERSTEL, Germany and Static Headspace module, Ionicon, Austria); HS-SPME-GC-MS (7890B GC system coupled to a 5977A MSD, Agilent, Little Falls, DE, equipped with an MPS Multipurpose Sampler, GERSTEL, Germany); and SHS-GC-IMS (FlavourSpec GC-IMS system, G.A.S., Germany, equipped with an HT2000H headspace autosampler, HTA, Brescia, Italy).

Data processing

For PTR-ToF-MS raw data deadtime correction, internal calibration of mass spectral data, and peak extraction were performed according to previously described procedures [5].

For GC-MS, data were acquired and processed with Agilent MassHunter. Target peaks were identified based on their MS spectra and linear retention index. Peak areas were calculated on the response of a target ion. Up to two qualifier ions were monitored to increase the reliability of the peak area extraction.

For GC-IMS automated untargeted data processing, the output files of the instrument were imported in R, the region containing peaks was selected and data reduction by binning was applied. After this pre-processing step, peak detection based on persistent homology was performed using the Python package findpeaks [6]. The reticulate [7] R package was used to integrate the Python code in R code. The intensities of the automatically detected peaks were extracted for each sample.

Results and Discussion

A targeted approach was employed to monitor key odorants (specifically filbertone) and roasting markers (alkyl pyrazines), revealing distinct evolution patterns. For instance, the hazelnut key odorant, filbertone, exhibited higher abundance in "Tonda Gentile delle Langhe" hazelnuts throughout the entire roasting process. Simultaneously, untargeted strategies offered insights into the complex nature of the volatilome of roasted hazelnuts and its changes during thermal treatment. An automated peak detection workflow for GC-IMS data was developed and applied.

The synergistic use of multiple analytical techniques not only enhanced the reliability of analyte identification but also yielded more comprehensive results in terms of extracted information.

The study highlights, on one hand, the effectiveness of a combined approach for volatilome characterization, and, on the other hand, the feasibility of employing rapid analysis tools, combined with automated data processing, when preliminary investigation by GC-MS allows for the identification of relevant features.

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Online measurement with Proton Transfer Reaction Mass Spectrometry of two widely used herbicides in agriculture

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Abstract

The contamination of the atmosphere by pesticides used in agriculture to protect crops is well known. This contamination is partly due to the volatilisation of pesticides after application. However, volatilisation measurements are few. Therefore, there is a strong need to develop methods for continuously measuring the gaseous concentration of pesticides in ambient air and their emissions over a sufficiently long period to capture the entire volatilisation period. A proton transfert reaction mass spectrometer (PTRMS) has been used to measure the volatilization of 2 herbicides (Prosulfocarb and Pendimethalin) at high frequency on a bare soil. A permeation set up was developed to calibrate PTR-MS and study the effect of the humidity in the condition near ambient air.

Introduction

Pesticides are widely used in agriculture to protect crops from pests, weeds, and diseases, but they disperse into water, plants and the atmosphere. The contamination of the atmosphere is partly due to the volatilisation of pesticides after application, accounting for up to 90% of the application dose in some cases [2].

However, volatilisation measurements are scarce. Active air concentration measurements are usually based on solid adsorbent trapping techniques, requiring sampling periods of several hours. These campaigns, time consuming, are generally carried out over a few days. But the contamination of the atmosphere is observed during the periods of application but also afterwards. Therefore, there is a strong need to develop methods for continuously measuring the gaseous concentration of pesticides in ambient air and their emissions over a sufficiently long period to capture the entire volatilisation period at high frequency.

In this context, the OnlinePTR4pests project (funded by ADEME) aimed to measure pesticide concentration and volatilisation using proton transfer mass spectrometry (PTRMS). The main scope of this present work was to develop a method to calibrate 2 herbicides widely used in field crops: Prosulfocarb and Pendimethalin. Gas-phase calibration is a critical point in the development of PTR-MS measurements. In the absence of a standard gas available on the market, we have developed and tested a system for generating a known concentration of the molecules of interest, adapted from Vesin et al. [5]. The response of PTRMS to air humidity was then characterised in the lab. Finally, a 3-week field measurement campaign was carried out over bare soil, during which we quantified the concentrations of Prosulfocarb and Pendimethalin in the air using two analytical chains: PTRMS and a reference method by Thermo Desorption Gas Chromatography Mass spectrometry (TD-GCMS) already used to measured pesticides concentrations outdoor [3, 4].

Experimental Methods

Generation of known concentration by a permeation system

A permeation system was developed to generate the pesticide in gas phase at a known concentration: the pesticide was deposited in a micro vial hermetically sealed by a permeation membrane. A stream of 30 ml min^{-1} zero air was forced over the micro vial, then diluted by zero air at flow rates from 3 to 9 l min^{-1}. The device was made entirely of stainless steel and PFA tubing, with several air flow regulators, 2 water tanks and a thermoregulated oven. Two permeation temperatures were tested: 80 and 100°C. Permeation rates were determined by gravimetry, by weighing the loss of the pesticide in the micro vial.

Lab measurement and detection by PTRMS

Prosulfocarb and pendimethalin were detected by a proton-transfer quad-injection time-of-flight mass-spectrometer (PTR-Qi-TOF-MS, Ionicon, AU). After testing, the conditions were set as follows: H3O+ mode, inlet and drift temperature 120°C, drift pressure 4 mbar, E/N 132 Townsend, unless otherwise stated. The ratio E/N 88 and 110, inlet and drift temperature between 80°C and 120°C, ionization mode were tested. The calibration of the PTRMS was performed at 4 levels of humidity: 0, 20, 50 and 80% relative humidity. Water vapour concentrations were recorded with an infrared absorption gas analyser (LI-840A, Licor, USA). The PTRMS measurements were validated by comparison with the concentration measured by the well established TD-GC-MS method with an active sampling system placed in parallel to the PTRMS chain.

Field measurement

The experiment took place on the ICOS FR-EM2 site in the north of France (https://meta.icos-cp.eu/resources/stations/ES_FR-EM2) at the BioEcoAgro unit of INRAE in Mons. Wheat was sown on the plot on 26 October 2020 following shallow ploughing. The measurements were taken on a bare soil from 4 to 25 November 2020. Pesticides treatment took place on 5 November 2020 with a mixture of the following products : Minarix (Prosulfocarb at 800g/L) and Codix (Diflufenicanil at 40 g/L and Pendimethalin at 400 g/L) applied at 130 L ha^{-1}. The ambient air in the parcel was sampled at 1.6 m above the ground with a flow rate of 50 NL min^{-1}. The air was routed to a manifold regulated at 80°C via a 30 m ½ inch PFA tube also regulated at 80°C, before sampling by the PTR-Qi-TOF-MS at 500 mL min^{-1} through a 1.2 m long, 1/8 in. PFA tube heated to 120°C. The manifold was connected to a 50 Hz dry vane pump (Busch, SW).

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Results

Permeation system

Depending on the experiment (laboratory or field), pesticide mass loss within the permeation system was monitored over periods of 6 to 50 days, with weighing frequency varying from 1 to 7 days. An example of gravimetric monitoring carried out during the field experiment is shown for both compounds in Figure 1. A coefficient of determination R^2 0.98 is found for Prosulfocarb. However, there is a uncertainty in determining the permeation rate at short time scales: the rate differs by a factor of two if all the points are or only the last two weighings of the calibration of are used (16.5 +/-5% µgh^{-1} or 7.8+/-25% µg h^{-1} respectively). For Pendimethalin, the mean permeation rate was 0.94 +/-17% µgh^{-1} with a slightly lower coefficient of determination than Prosulfocarb ($R^2 = 0.89$). This is probably due to the precision of the balance being closer to the weights differences to measure. The device of the permeation system with the associated dilution system could generate concentrations from 0.5 to 7 ppb of Prosulfocarb and from 0.040 to 3 ppb of Pendimethalin. Measurements of Pendimethalin concentration by the independent method GCMS, was used to validate the permeation system. We found an agreement within a factor from 1 to 2.2 which can be explained by the uncertainty on the permeation rate.

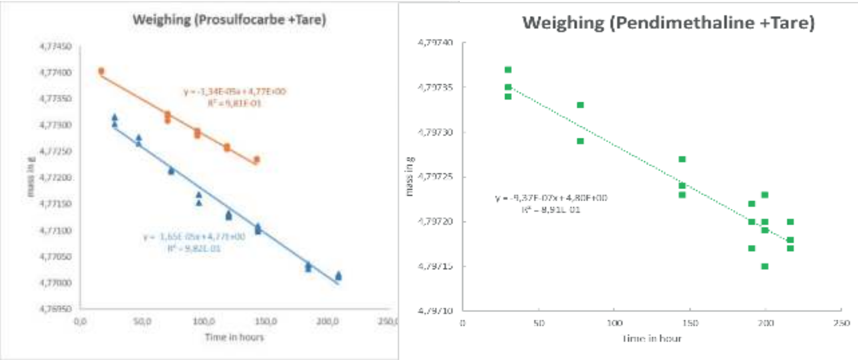

Figure 1: Weight of pesticide mass within the permeation system as a function of time (left) Prosulfocarb and (right) Pendimethalin. The equation slope gives the permeation rate.

PTRMS Calibration

The dilution module, made up of two flow regulators and a mixing cell, was used to generate variable pesticide concentrations by varying the diluent air flow. Figure 2 shows, under dry conditions, a very strong correlation between the PTR-Qi-TOF-MS signal and the Prosulfocarb concentrations generated by the permeation-dilution system. The same linearity was observed with Pendimethalin. These very good regressions indicate, on the one hand, that the dilution system generates a very satisfactory concentration range and, on the other hand, that the PTR-Qi-TOF-MS responds linearly to variable concentrations for the 2 pesticides. In addition, the isotopes of Prosulfocarb can be used successfully to improve the accuracy of estimates of low concentrations as in ambient air.

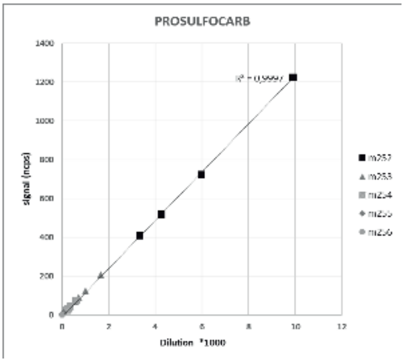

Figure 2: PTR-Qi-TOF-MS signal in normalized counts per second (ncps) as a function of the dilution applied (i.e proxy of Prosulfocarb mixing ratio generated by the permeation-dilution system) under dry conditions. The m/z 252 is the main isotope of Prosulfocarb, while other masses belong to the isotopic massif.

Humidity dependence of concentration measurements

The effect of air relative humidity on concentration measurement is different for the two tested pesticides. Figure 3 shows a strong humidity dependence for Prosulfocarb. The higher the relative humidity, the higher the PTR-Qi-TOF-MS signal (ncps), with a factor around 4 between RH=80% and RH=0%. In contrary, for Pendimethalin the PTR-Qi-TOF-MS signal decreased slightly when RH increased. This effect appeared to be strong between 0 and 20% humidity but not significant between 20 and 80% RH.

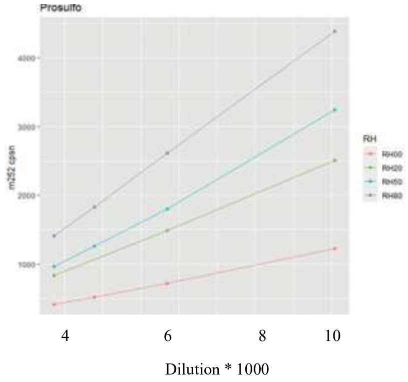

Figure 3: PTR-Qi-TOF-MS signal in ncps as a function of the Prosulfocarb concentration at various relative humidity (RH).

Discussion

In conclusion, we succeed to generate Pendimethalin and Prosulfocarb in gas phase with the permeation system in a concentration range corresponding to environmental conditions. However, variations in the generated rate require a frequent determination and will need further investigations. The effect of humidity on concentration requires further investigations to determine if water clusters and fragments may explain the observed behaviours [1, 6].

It has to be noticed that the concentration generated are near environmental conditions and are very well detected by PTRMS. Because of the dependence on humidity, mainly Prosulfocarb ambient air concentrations will have to be corrected as a function or relative humidity of the air. The measurements by both GCMS and PTRMS should be able to validate this correction.

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PTR-MS as a CIMS? Increasing the Range of Detectable Compounds via Low Pressure Negative Soft Chemical Ionization

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Abstract

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a soft chemical ionization technique to quantitatively detect volatile and condensed organic compounds on a chemical composition level.

We recently introduced a next generation PTR-MS, the so-called FUSION PTR-TOF 10k, which merges the advantages of a pristine and well-studied ion-chemistry of a traditional PTR-MS with the high sensitivities and low limits of detection (LOD) of a near-atmospheric pressure chemical ionization mass spectrometer (CIMS).[1] With LODs well below the pptV range, a significantly improved decoupling of the ion-source with the FUSION reaction chamber reducing ionic and neutral interferences and a high resolution TOF-MS (up to 15,000 m/Δm), FUSION PTR-TOF 10k is predestined to study complex mixtures of SOA and respective gas-phase precursors.

However, positive chemical ionization with H_3O^+, NH_4^+, NO^+, and O_2^+ mostly limits the application of PTR-MS to organic compounds (with some exceptions like HNO_3 or NH_3).

For this work, the instrument was equipped with bipolar electronics, capable of switching polarity within seconds. A complete redesign of the FUSION ion-molecule reactor allows operation in a reduced pressure CIMS-like tradition: no drift voltage is applied; ions are solely controlled by RF voltages applied to a series of ring-electrodes.

Together with the novel Fast-SRI ion source, negative primary reagent ions like CO_3^- and I^- are now additionally accessible, without the need for any hardware modifications. This increases the range of detectable compounds to inorganics like SO_2 with 1-min LODs in the single digit pptV range. But also, other small acids and halogenated compounds become detectable.

The ionization scheme of CO_3^-, for example, with SO_2 is as follows as has been described earlier by Möhler et al. (1992):[2]

$$CO_3^- H_2O + SO_2 \rightarrow SO_3^- * H_2O + CO_2$$

$$SO_3^- + O_2 + M \rightarrow SO_5^- + M$$

Here, we present results from a thorough characterization of the new CO_3^- ionization mode based on pure chemicals. Figure 1 shows a comparison of the fragmentation in CO_3^- and H_3O^+ mode. As a further example, the quantification of SO_2 in ambient air in the city of Innsbruck will be presented.

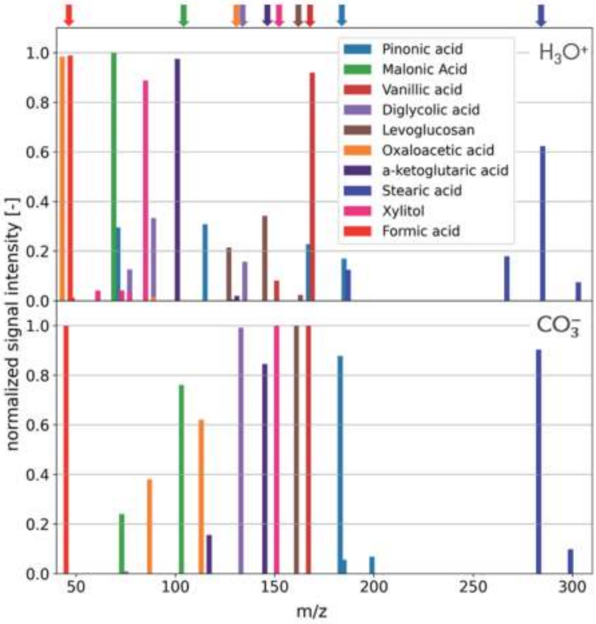

Figure 1: Comparison of pure chemicals detected CO_3^- with mode in the lower panel, and in H_3O^+ mode in the upper panel. CO_3^- ionization is most selective to acids and ionic fragmentation is significantly reduced. Arrows on top of the figure indicate the position of the neutral mass of each compound.

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Gas and particle-phase volatile organic compounds measurements over urban area in Munich during summer time

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Abstract

To obtain a comprehensive understanding of the sources, chemical composition, and concentrations of volatile organic compounds (VOC) in Munich, the most prosperous city in Germany, during the summer time. We used a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) coupled with a particle inlet (CHARON) to measure VOC concentrations and the chemical compositions of aerosol particles alternatingly in real time. An aerosol mass spectrometer (AMS) was utilized to measure the size-resolved chemical composition of non-refractory aerosol particles. Positive matrix factorization (PMF) is used to identify the sources of VOCs and organic aerosol particles (OA). Seventy two percent of the $PM_{2.5}$ mass concentration on average was composed of secondary organic aerosol (SOA). Results from this research contribute valuable information for controlling the emissions of VOCs and SOA in urban areas.

Experimental Methods

Measurement Site

During the summer of 2023 (August 3rd to August 29th), field measurements took place in downtown Munich, Germany. Munich, the capital of Bavaria, has a population of approximately 1.6 million, with its metropolitan area home to about six million people. The city is situated along the River Isar, just north of the Alps. Our measurements were carried out at a specific site in front of the Ludwig Maximilians University (LMU) Munich's Institute of Mathematics, strategically situated in the heart of the city. This central location is characterized by its proximity to numerous restaurants. The predominant wind patterns at this site primarily originate from the southwest direction. As a result, local air quality is subject to various influences, including factors such as urban traffic, biomass burning, and, depending on meteorological conditions, emissions from both anthropogenic and natural sources in the vicinity, which can be transported over a regional scale.

Instrumentation

In our research, we employed a range of advanced instruments to assess air quality and aerosol composition, including a high-resolution time-of-flight AMS for NR-$PM_{2.5}$ analysis, OPC for particle size and mass concentration measurements, CPC to determine particle number concentrations, and aethalometers for Black Carbon (BC) monitoring. Additionally, we used a PTR-MS system with a CHARON inlet for real-time analysis of VOCs and semi-volatile aerosol components. We also measured trace gases like ozone (O_3) and nitrogen dioxide (NO_2). Meteorological parameters were recorded with a compact sensor and supplemented with wind data from the LMU meteorological department. These instruments collectively provided valuable insights into air quality and aerosol dynamics.

Results

Figure 1 indicates that the values of AMS combined with Black Carbon closely match the values of PM2.5. These findings suggest that the primary constituents of PM2.5 are organic aerosols.

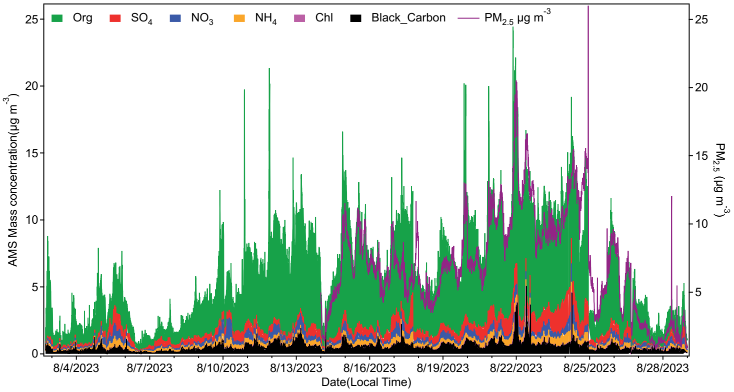

Figure 1: $PM_{2.5}$ mass concentrations obtained from Fidas-OPC and NR-$PM_{2.5}$ from AMS organics (Org), sulfate (SO_4), nitrate (NO_3), ammonium (NH_4) and chloride (Chl) and black carbon (BC) in summer 2023

Cross-correlations of Biogenic Volatile Organic Compounds (BVOC) emissions typify different phenological stages and stressful events in a Mediterranean Sorghum plantation

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Abstract

Climate change will impact the growing season and increase extreme stressful events, affecting crop phenological phases and the emission of biogenic volatile organic compounds (BVOC). This study conducted continuous measurements of BVOC fluxes and CO2 net ecosystem exchange (NEE) throughout a growing season in a Southern European grain sorghum plantation. The results revealed that the sorghum plantation emitted oxygenated BVOC, mainly methanol and acetaldehyde, at average rates of 0.137 ± 0.013 and 0.070 ± 0.004 nmol m−2 s−1, respectively. Self-Organizing Maps (SOM) identified distinctive BVOC flux patterns correlating with sorghum growth stages (GS). During GS1, developing plantlets emitted monoterpenes; in GS2, adult plants with a dense canopy emitted abundant oxygenated BVOC, including methanol, acetaldehyde, formic acid, acetone, acetic acid, and n-pentenol. In GS3 (flowering stage), only a few BVOCs continued to be emitted at high rates. SOM applied to a subset of BVOC fluxes differentiated stressful events such as plant lodging and harvest cutting, with enhanced acetaldehyde emission distinguishing lodged sorghum plants.

Introduction

Climate change is expected to impact crops by altering phenological phases or shifting the entire growing season, making agricultural ecosystems more challenging to manage. This is particularly relevant in the Mediterranean basin, where increased stressful environmental conditions are anticipated, leading to a negative effects on potential crops yields, because of a reduced CO_2

photosynthetic assimilation. Plants utilize assimilated CO_2 to synthesize and emit biogenic volatile organic compounds (BVOC), crucial for ecosystem interactions. The micrometeorological method of eddy covariance, coupled with Proton Transfer Reaction 'Time-Of-Flight' mass spectrometry, is used for real-time quantification of BVOC fluxes. While most field campaigns focus on forests, this study examines BVOC exchanges in a Southern European grain Sorghum plantation throughout a growing season. The research used Self-Organizing Maps (SOM) to explore long-term correlations between BVOC fluxes and physiological/environmental variables. The identification of these relationships could assist in monitoring crop development and diagnosing stressful events, aiding decision-making for sustainable agriculture.

Experimental Methods

Site description

The experimental field site is situated in a farm in Eboli, Italy, within the ICOS (Integrated Carbon Observation System) network, with a typical Mediterranean climate with hot and dry summers and cool, rainy winters. Measurements were conducted from June 1 to August 23, 2018. Prior to the sowing date on June 17, soil ploughing and ripping activities took place. Sorghum grain was sown with a density of 70 kg/ha and approximately 200 plants per square meter, emerged on June 24 and harvested from August 5 to 21. Growing season was divided into four fixed stages (GS). Irrigation was applied with a central pivot system.

PTR-TOF BVOC measurements and computation of Eddy Covariance Fluxes

A Proton Transfer Reaction “Time-of-Flight” Mass Spectrometer (PTR-TOF-MS 1000, Ionicon, Innsbruck, Austria) continuously measured the concentration of a wide range of biogenic volatile organic compounds (BVOC) at a frequency of 10 Hz. The instrument operated under controlled conditions resulting in a protonation energy (E/N) of ~122 Td. Background signals were automatically measured four times a day, with BVOC-free air. Post-processing was performed using the PTR-TOF Data Analyzer. Mass scale calibration utilized well-defined ion peaks. Focus was placed on 23 protonated ions relevant to plant growth and stress, selected from the mass range of m/z = 0 to m/z = 280. A custom-made Matlab routine program performed background subtraction, correction for ion fragmentation, despiking and converted signal to concentrations (ppbv) using a theoretical calculation. Key BVOC s fluxes were determined using the Eddy Covariance technique, coupling a 3-D sonic anemometer with PTR-TOF-MS to measure wind speed. Data from both instruments were synchronized and fluxes of CO_2 and H_2O were also measured with an infrared gas analyzer (IRGA). Air was drawn through a PFA sampling line with an aspirating pump to maintain a turbulent flow. BVOC fluxes were calculated using EddyVoc. A lag-time window of 2.5–5.5 s was used to optimize BVOC flux calculations and a constant time-lag, using methanol as a reference was used. Random uncertainty and limits of detection (LoD) were calculated for each flux, with 9 to 31% of fluxes above the LOD. Median values of BVOC fluxes during central hours of the day were used to calculate basal emission factors (BEF).

Self-organizing map (SOM)

The Self-Organizing Map (SOM) is an unsupervised neural network machine learning algorithm. It transforms high-dimensional data with non-linear statistical relationships into simple geometric relationships on a two-dimensional component plane. SOM was utilized to cluster, explore and visually represent correlations among time-series of BVOC fluxes, environmental variables (Tair, PAR, VPD), net ecosystem exchange (NEE), and growth indexes (GAI, AGB).

Results and Discussion

BVOC exchange across phenological stages and Basal Emission Factors (BEF)

BVOC fluxes over the sorghum crop unfolded four distinct growth stages (GS0 to GS3). In the initial stage (GS0) the field was considered bare soil until sorghum plantlets emerged at the end of this phase on June 24th. Negligible values of GAI and AGB accompanied a median positive flux of NEE in GS0 (6.75 µmol m^{-2} s^{-1}), indicating soil respiration. In GS1, active sorghum growth was evident, marked by increasing GAI and AGB, coupled with high net photosynthetic CO_2 uptake and a median NEE flux of -3.99 µmol m^{-2} s^{-1}. GS2 showed the end of vegetative growth, with the highest GAI (17.30 ± 1.70 m^2 m^{-2}) at reproductive phase onset, resulting in a median NEE of 4.69 µmol m^{-2} s^{-1}. GS3 coincided with sorghum senescence, demonstrating by the highest NEE (7.07 µmol m^{-2} s^{-1}). Throughout these stages, evapotranspiration flux remained stable, and daily median air temperature (~25 °C) slightly increased from GS0 to GS2, with high Photosynthetically Active Radiation (PAR). Methanol was the most emitted BVOC, averaging 0.137 ± 0.013 nmol m^{-2} s^{-1} over the season. Weekly methanol fluxes peaked in GS3 at 0.216 nmol m^{-2} s^{-1}. Acetaldehyde, emitted at an average rate of 0.070 ± 0.004 nmol m^{-2} s^{-1}, exhibited similar diurnal patterns as methanol in GS2 and GS3. Emissions of formic acid, acetone and acetic acid showed higher rates in fully developed stages (GS2 and GS3). Protonated ion m/z = 69.069 showed ambiguous identification but increased from GS1 to GS2. Additionally, two Green Leaf Volatiles (GLVs), cis-3-hexenol, and trans-2-hexenal, were emitted in GS2. Monoterpenes exhibited positive median rates mainly in GS1. BEF calculations showed notable seasonality, with monoterpenes and m/z = 69.069 displaying the highest variation. Stressful events like lodging and harvesting operations amplified BVOC emissions, particularly methanol, acetaldehyde and formic acid. Two lodging events occurred between July 23rd-29th and August 15th-19th. These events involved sorghum plants bending. The second lodging coincided with harvesting operations from August 5th-10th, covering 55% of the footprint area. Both lodging and cutting triggered peak emissions of BVOC. In the first lodging, acetaldehyde was the predominant BVOC, with a median rate of 0.042 nmol m^{-2} s^{-1}, peaking at 0.518 nmol m^{-2} s^{-1}. Formic acid, acetone, acetic acid and m/z 69.069 were emitted to a lesser extent. The second lodging induced significant methanol emissions (0.595 nmol m^{-2} s^{-1}), followed by formic acid (0.179 nmol m^{-2} s^{-1}) and acetaldehyde (0.128 nmol m^{-2} s^{-1}), doubling compared to the first lodging. The proximity of these events led to a prolonged release of BVOC post-cutting. Stressful events like lodging and initiation of cutting and harvesting significantly enhanced oxygenated BVOC emissions in GS2 and GS3. Stem lodging, a consequence of plants bending over, led to a shading effect on other plants, triggering acetaldehyde emission.

BVOC correlation with GS, environmental variables and stressful events with SOM

Throughout the sorghum growing season, BVOC, NEE, environmental variables and sorghum growth indexes, were subjected to SOM algorithms, which revealed distinctive patterns correlated with different phenological stages. In the SOM (Fig. 1) a red-labelled area near the bottom-left corner showed high emissions of methanol, acetaldehyde, formic acid, acetone, acetic acid and m/z 69.060. This clustering was prominent when Tair, PAR, VPD reached peak levels, indicating a significant dependence on these environmental variables. Furthermore, the highest emission rates of oxygenated-BVOC and m/z 69.060 aligned with the high AGB and GAI and negative NEE, particularly during the GS1 to GS2 transition. In the bottom-right corner, another cluster emerged, characterized by high negative NEE, AGB, and medium to high GAI, highlighting the GS1. Additionally, high emissions of selected oxygenated-BVOC (formic acid, acetone, acetic acid), m/z 69.060, and GLVs were grouped on the right side component planes, correlated with high levels of

AGB and GAI, positive NEE and mid-low PAR, particularly during the GS3. Focusing the SOM on a data subset from lodging and cutting (Fig. 2), the highest methanol fluxes clustered on the top-right corner, along with high emissions of formic acid and acetone. Another cluster with the highest acetaldehyde emissions, located on the top-left corner, showed a relationship with high emissions of formic acid, acetone, and m/z 69.069. These findings contribute to a comprehensive understanding of BVOC dynamics during the sorghum growing season and highlight specific correlations during stress-induced events.

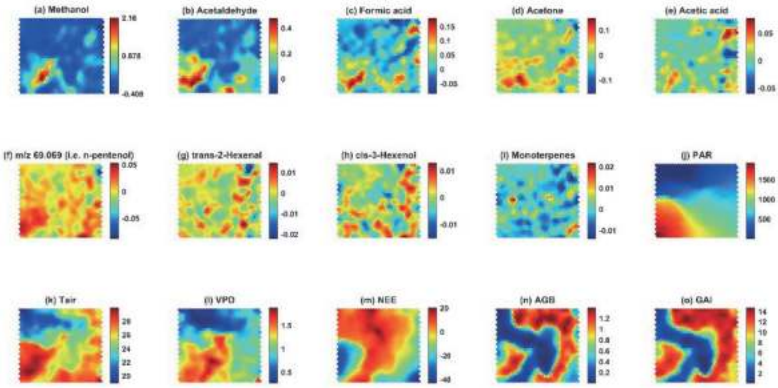
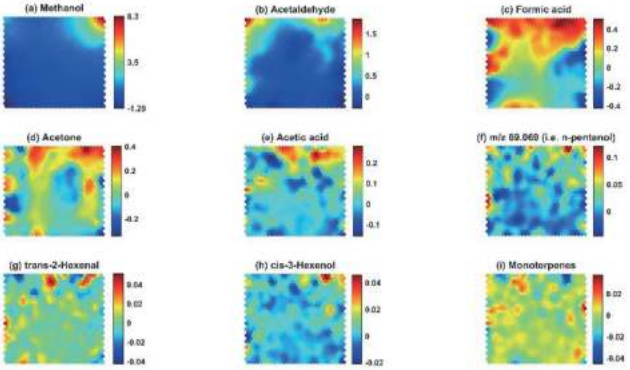

(a) Methanol
(b) Acetaldehyde
(c) Formic acid
(d) Acetone
(e) Acetic acid
(f) m/z 69.069 (i.e. n-pentenol)
(g) trans-2-Hexenal
(h) cis-3-Hexenol
(i) Monoterpenes
(j) PAR
(k) Tair
(l) VPD
(m) NEE
(n) AGB
(o) GAI

Figure 1: Panels (a–o) are component planes of the SOM for fluxes of BVOC (a–i), PAR (j), Tair (k),VPD (l),NEE (m), AGB (n), (GAI) (o). On the planes the lowest measured values are dark blue and the highest are dark red.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(h) cis-3-Hexenol
(i) Monoterpenes

Figure 2: Panels (a–j) are component planes of the SOM for fluxes of BVOC measured during the occurrence of both plants lodging (23rd - 29th of July and 15th - 19th of August 2018) and the beginning of harvest cutting (5th - 10th of August 2018). On the SOM-planes the lowest measured values are dark blue and the highest are dark red.

Real-time air concentrations and turbulent fluxes of Volatile Organic Compounds (VOCs) over historic closed landfills to assess their potential environmental impact

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Abstract

For the first time, real-time monitoring of VOCs was performed over a historic closed landfill site in southern Italy by Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS), to assess their emission fluxes by Eddy Covariance (EC). Two field campaigns of one week were performed in July and October 2016, where concentrations and fluxes of CO_2 and CH_4 were also measured. Many compounds not previously identified in the biogas from the site, such as methanol, some carbonyls, sulfur compounds and organic acids, were detected by PTR-TOF-MS. Only in July some of them produced positive fluxes that, although small, largely exceeded the flux limit of detection. Methanol was the most emitted compound with an average flux of 44.20 ± 4.28 $\mu g\ m^{-2}\ h^{-1}$, followed by toluene with a mean flux of 18.97 ± 2.47 $\mu g\ m^{-2}\ h^{-1}$. Toluene fluxes were 10 times higher than those of benzene, fitting rather well with values previously measured in the biogas. No relevant VOC fluxes were measured in October, suggesting that temperature was the variable controlling most landfill emission. VOCs emission fluxes often reflected the biogas composition, such as for benzene and toluene; conversely for monoterpenes, this was not observed. This, combined with tiny emissions of VOC oxidation products, suggested that landfill emissions underwent some photochemical degradation before being dispersed in the atmospheric boundary layer (ABL). Accumulation in the ABL led to deposition fluxes of some VOCs emitted from the sea. Our results show that, albeit small, summer emissions from the studied landfill can certainly have an impact on the population living nearby, because they contain or still generate compounds that cause nuisance.

Introduction

Little is known about the potential environmental impact of historic closed landfills, due to difficulties to assess the fugitive emission rates of volatile organic compounds (VOCs). Despite VOCs are a small portion of total biogas content, they are emitted from these landfills due to leaks in pipelines and cracks in the insulating cap. The concern is related to the potential production of VOCs and sulfur compounds, particularly if illegal dumping of toxic waste has occurred. The study introduces a novel approach using Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) combined with Eddy Covariance (EC) to estimate real-time fluxes of VOCs and hydrogen sulfide (H_2S) from the Giugliano municipality historic closed landfills. VOCs, CO_2, and CH_4 fluxes measurements, were conducted in July and October 2016.

Experimental Methods

Study area and meteorological measurements

The study area comprises the historic closed Giugliano landfills in the Campania region, with a Mediterranean climate characterized by hot summers and mild winters. The landfills are located in a flat area surrounded by agricultural land and tree orchards, contributing to biogenic volatile organic compounds (VOCs) emissions. High ozone (O_3) levels are typical during hot seasons. Local anthropogenic VOC sources include traffic emissions, heating appliances, industrial combustion and solvent use, mainly concentrated in urban areas. Six historic landfills, categorized into two clusters based on age and waste type, were investigated. Continuous monitoring of VOCs and inorganic compounds was conducted during high and low biogas emission periods in July and October 2016. Meteorological data, including temperature, humidity, wind speed, and solar radiation, were collected. O_3 levels were monitored in regional air quality stations.

Experimental set-up: PTR-TOF-MS data processing and EC fluxes calculation

The study employed a PTR-TOF-MS 1000 from Ionicon for detecting VOCs across a wide mass range, acquiring signals at a frequency of 10 Hz. The experimental setup and data processing mirrored those described by Manco et al. (2021), with site-specific adjustments. PTR-TOF-MS generated 6-minute raw data files, post-processed using the PTR-TOF Data Analyzer. Monitoring focused on 40 compounds within the mass range of $m/z = 0$ to $m/z = 350$. A custom Matlab program performed background subtraction, ion fragmentation correction and despiking. It converted signal intensities to mixing ratios through theoretical calculations, confirmed by calibrating with a standard gas mixture. Eddy covariance fluxes were computed determining covariance between air concentration (C) and vertical wind speed (w). Fast-response sensors captured small-scale eddy contributions at the site, housed on 30-meter tower, including an ultrasonic anemometer, open-path gas analyzers, and the PTR-TOF-MS sampling line. An aspirating pump maintained turbulent flow. Gas mixing ratios were logged at 10 Hz on synchronized computers. EddyPro software calculated CO_2 and CH_4 fluxes while EddyVOC computed VOC fluxes. Quality control was applied and EC fluxes limit of detection (LOD-EC) established the smallest detectable flux.

Results and Discussion

Meteorological conditions during the monitoring campaigns

In July, high atmospheric pressure and warm temperatures prevailed, driven by sea breezes in the afternoon activated after 10 AM and peaked around 1 PM, coinciding with maximum O_3 values. The stable surface layer developed after sunset and persisted overnight, disrupted only by turbulent mixing and advection from the sea. October showed more variable meteorological conditions with increased rainfall, lower atmospheric pressure and reduced solar radiation intensity.

Concentrations of major inorganic gases and VOCs

CO_2 abundance in biogas suggested its use as a landfill emission tracer. In July, CO_2 displayed a diurnal cycle, peaking in the early morning and reaching a minimum around late afternoon. CH_4 profiles mirrored CO_2. Additional VOCs, beyond those identified by Carriero et al. (2018), were detected by PTR-TOF-MS. While some (e.g., methanol, acetone, toluene) exceeded 5 µg m^{-3} on average, most (e.g., formaldehyde, acetonitrile) rarely exceeded 1 µg m^{-3}. Benzene, toluene, and other compounds followed dynamics similar to CO_2 and partly CH_4. The toluene/benzene ratio (>10) matched landfill emission characteristics. Compounds affected by sea advection, such as acetone, showed high concentrations, occasionally exceeding 73 µg m^{-3}. Formaldehyde, acrolein, and other compounds were measured, possibly originating from landfills or photochemically polluted plumes. Diurnal variations in isoprene, H_2S, methylmercaptan, and DMS were observed. In October, CO_2 diurnal variations were similar to July, with stronger peaks due to increased rain events. Isoprene concentrations exceeded summer levels, indicating contributions from broadleaved forests. Wind changes minimally affected formic acid but influenced acetic acid and DMS, suggesting marine origins. Methylmercaptan concentrations follow arene trends. H_2S concentrations mirrored July but did not precisely align with CO_2 and CH_4 peaks.

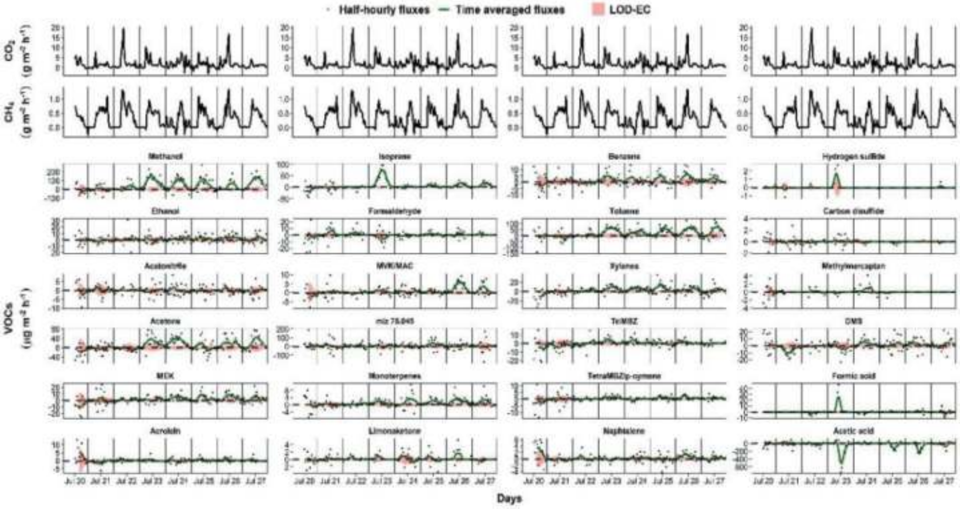

Figure 1. Time-series of CO_2 (µg m^{-2} h^{-1}), CH_4 (µg m^{-2} h^{-1}) and main VOC fluxes measured (µg m^{-2} h^{-1}) from 20th to 27th of July, 2016. Black points show halfhourly fluxes, green lines time averaged fluxes and the shaded red area represents the limit of detection (LOD) of VOC fluxes.

Fluxes of VOCs and other trace gases

Both July and October campaigns showed positive fluxes of CO_2 and CH_4, indicating regular diurnal biogas emissions from landfills, occurring mainly in bursts. In July, numerous volatile compounds displayed positive fluxes exceeding the LOD-EC, with regular fluxes of arenes observed from around 11 AM to 6 PM. Toluene exhibited the highest mean positive flux (18.97 ± 2.47 µg m^{-2} h^{-1}), ten times higher than benzene. Methanol emerged as the most emitted compound, with an average flux of 44.20 ± 4.28 µg m^{-2} h^{-1}. Regular emissions of acetone, MEK, and episodic emissions of ethanol, acetonitrile, and acrolein were also observed. Isoprene, formic acid, and H_2S exhibited episodic emissions, particularly on July 23rd, coinciding with high CO_2 and CH_4 levels. October showed daily CH_4 emissions, shorter than in July, and influenced by temperature. Arene, alcohol, isoprenoid, carbonyl, and sulfur compound fluxes were generally small. Toluene and methanol had lower emission fluxes, emphasizing strong seasonal variability. Alternating sea and land advection resulted in lower acetic acid and DMS deposition. Lower VOC emission fluxes in autumn relative to CO_2 and CH_4 suggested temperature has more severe impact on VOC production, evaporation and diffusion, making CO_2 and CH_4 unsuitable proxies of landfills VOC emissions.

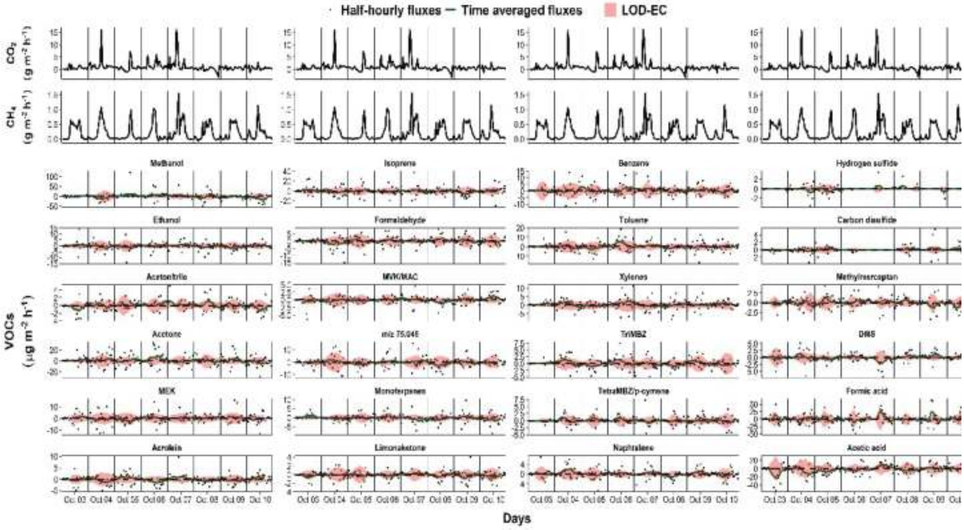

Figure 2. Time-series of CO_2 (µg m^{-2} h^{-1}), CH_4 (µg m^{-2} h^{-1}) and main VOC fluxes measured (µg m^{-2} h^{-1}) from 3rd to 10th of October 2016. Black points show halfhourly fluxes, green lines time averaged fluxes and the shaded red area represents the limit of detection (LOD) of VOC fluxes.

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Challenges of measuring isoprene oxidation products with a chemical ionization mass spectrometer

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Abstract

Isoprene is a volatile organic compound (VOC) emitted by plants and plays a crucial role in atmospheric chemistry. Its atmospheric oxidation pathways, particularly the OH oxidation pathway, are well-established. Here we show that accurate measurements of isoprene oxidation products still remain challenging. Even instruments using soft ionization methods are fragmenting the peroxy-radicals produced from isoprene OH oxidation. Isoprene oxidation product consist of different isomers, which makes an exact analysis additionally complex. Using isotopically labeled oxygen (^{18}O), we demonstrate the formation of at least one more $C_5H_8O_3$ isomer besides HPALD in the isoprene oxidation pathway. These findings highlight the complexity of isoprene reaction pathways and their implications for atmospheric processes. Accurately predicting the fate of isoprene and its oxidation products in the atmosphere impacts human health and climate change.

Introduction

The VOC (volatile organic compound) isoprene is a hydrocarbon with two conjugated double bonds. The annual global emission of isoprene is estimated to be 540 tera-grams per year. It is mainly emitted from broadleaf plants into the atmosphere [1].

The isoprene oxidation pathways involving reactions with OH, O_3, NO_3, and Cl radicals are well known. We focus on the OH oxidation pathway, which is the prevailing mechanism during daylight hours when about 90 % of isoprene reacts with OH radicals. A nearly complete gas-phase oxidation mechanism and a simplified version for chemical transport models is presented in the very detailed review “Gas-Phase Reactions of Isoprene and Its Major Oxidation Products” from Paul Wennberg et al. [3] Oxidation of isoprene leads to various products with functional groups that contribute to SOA formation.

However, there are a lot of challenges to measure the oxidation products of isoprene. Previous studies investigated the conversion of hydroperoxides from isoprene oxidation (ISOPOOH) to carbonyls (methyl vinyl ketone MVK and methacrolein MACR) upon contact with stainless steel surfaces as is the case in many field and laboratory instrumentation. These conversions lead to an observational bias towards urban conditions. [4]

Experimental Methods and Discussion

In addition to those already known difficulties, further hurdles arise in measuring isoprene oxidation products. Highly oxidized isoprene oxidation products have a low vapor pressure and are lost in the inlet systems of instruments which are not wall contact free or optimized for high inlet flow. [5]

Measuring highly oxidized isoprene oxidation products utilizing the H_3O^+ mode as reagent ions leads to fragmentation. [6] Here we show that fragmentation of the OH isoprene peroxy radicals occurs by using even the soft NH_4^+ mode as primary ions. In a wall free flow reactor experiment, oxidizing isoprene by OH, we discovered fragmentation of the radical $C_5H_9O_3$ formed from isoprene oxidation towards C_5H_9O by conducting an extraction ramp. *[Figure 1]*

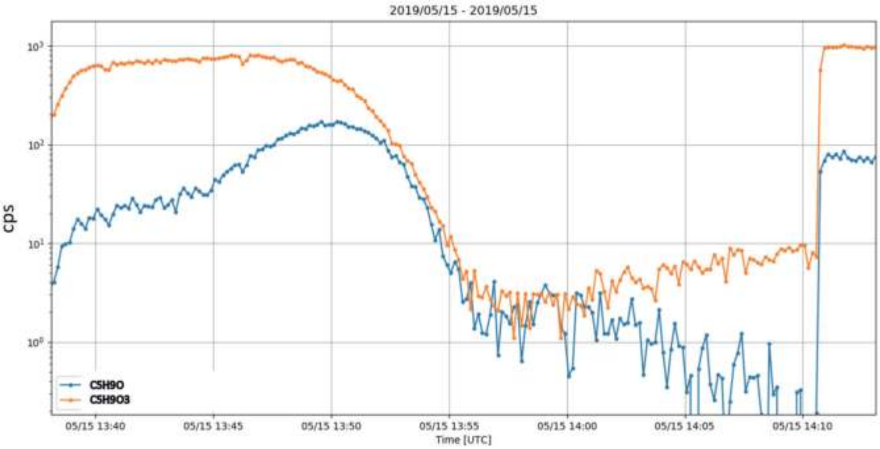

Figure 1: An extraction ramp during isoprene oxidation in a flow reactor experiment reveals fragmentation of the radical $C_5H_9O_3$ formed from isoprene oxidation to C_5H_9O measured in NH_4^+ mode.

Isomers additionally complicate the analysis of isoprene oxidation products. The isomers MVK and MACR or ISOPOOH and IEPOX in the isoprene oxidation pathway are already known [7].

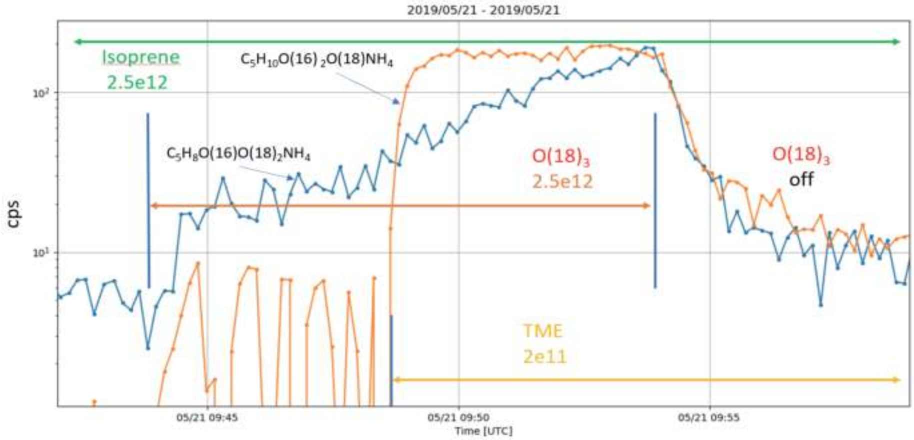

Figure 2: We used isotopically labelled oxygen to show the two different $C_5H_8O_3$ isomers in an isoprene oxidation flow reactor experiment.

Furthermore, we can show that there exists at least one additional C5H8O3 isomer besides HPALD also produced in the oxidation pathway of isoprene. Flow reactor measurements with isotopically labelled oxygen (18O) revealed that. It is likely, that this C5H8O3 isomer is produced from isoprene and ozone at the surface. [Figure 2]

Conclusion

The isoprene reaction pathways are complex, but the oxidation products have significant implications for atmospheric processes. The mentioned challenges and insights presented in here are essential for accurately predicting the fate of isoprene and its oxidation products in air quality and climate modeling.

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Preserving freshness by smart logistics: PTR-MS applications to monitor bell peppers quality decay through VOCs emissions

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Abstract

Focused on green sweet bell peppers, the research evaluates the effectiveness of the BulkBox (BB) in preserving the quality of green sweet bell peppers during the post-harvest stages of transportation and storage. PTR-TOF-MS was applied together with other sensory and instrumental methods for monitoring volatile organic compounds (VOCs) and ethylene emissions during refrigerated and room temperature shelf life up to 21 days. The findings emphasize the positive performance of the BB as a valuable tool for enhancing the shelf life of bell pepper and the PTR-TOF-MS utility in providing valuable insights into the dynamic changes of quality markers making it an indispensable tool for assessing and enhancing the postharvest preservation of fresh produce.

Introduction

Sweet peppers (*Capsicum annuum L.)* are an important food crop internationally, highly appreciated for its tasty flesh and peculiar long shape. They can be consumed fresh or processed, as unripe (green or white) or ripe (red, yellow and orange) fruits. While worldwide the production of this crop has increased in recent years and despite its relatively long shelf life, the annual losses of this crop are estimated to be 40% [1]. When stored at their optimal conditions (7-10°C, 95-98% RH), bell peppers have a shelf life of approximately two to three weeks [2] but changes in storage temperature and relative humidity can lead to quality degradation such as shriveling associated with water loss. Inside the project "SISTERS - Innovative systematic interventions for a sustainable reduction of food waste in Europe" (Horizon 2020, Grant Agreement No. 101037796), a smart container - the BulkBox (BB) – has been developed to reduce food losses and quality degradation during transportation and storage by exploiting passive modified atmosphere and the implementation of a sensor kit to monitor products' conditions in real time (*e.g.* CO_2, O_2, temperature and relative humidity).

In this work, different quality indicators, including volatile organic compounds (VOCs) emissions were monitored to validate the BB efficacy in better preserving the freshness of green sweet bell peppers (cv. *Lamuyo*) than conventional approaches for bulk transportation. Three different refrigerated transportations from Spain to Italy (1700 km) of realistic product quantities (200-300 Kgs) were performed, followed by shelf-life experiments. BB performance during shelf life was compared to regular transportation conditions by combining sensory and instrumental measurements of bell peppers including water loss, dry matter, texture parameters, color, appearance and VOCs emissions by PTR-ToF-MS and GC-MS.

Experimental Methods

Bell peppers were harvested in Spain and stored for 5 days at refrigerated temperature (7°C) before being shipped through a refrigerated truck to Edmund Mach Foundation (Italy). After receiving the products, shelf-life experiments were conducted at two different conditions: refrigerated (T=7°C, RH=90-95%) and ambient conditions (T=20°C, RH not controlled) to simulate supply chain operations. Two different types of PTR-TOF-MS measurements were realized during the shelf life: respiration rates and headspace analysis.

For respiration rates, 3 different peppers were sampled from each batch in different days (0, 2, 6, 9, 14 and 20). Samples were left at room temperature for at least 3 hours to allow equilibration. They were then put in a 1L glass jar hermetically closed for 30 minutes before being measured. For headspace analysis, samples were collected during the same days, grinded into frozen powder by using liquid nitrogen and conserved at -80°C till the day of the analysis. When analyzed, samples were inserted into 20 mL glass vials equipped with PTFE/silicone septa and mixed with an antioxidant solution before being measured through an adapted GC autosampler (MPS Multipurpose Sampler, GERSTEL). All samples were incubated at 40°C for 25 minutes for headspace equilibration, then measured for 50 seconds with an acquisition rate of one spectrum per second. A waiting time of 2 minutes was used for avoiding memory effects. The measurement order was randomized and empty vials were used as blanks. All the measurements were performed with a PTR-ToF-MS 8000 apparatus equipped with an ion funnel (Ionicon Analytik GmbH, Innsbruck, Austria) with H_3O^+ as primary ion. The Selective Reagent Ion mode was also used with O_2^+ as primary ion mode to collect data about ethylene emissions during the respiration rates measurements. Data deadtime correction, internal calibration and extracftion were performed through TOFOffice. Both multivariate statistical data analysis (*i.e.* PCA) and univariate data analysis (*i.e.* 1-way AOV followed by post-hoc tests) were used to investigate changes in the volatilome during storage and the treatment effect (BB *vs* standard). Mass peaks correlations with the other quality measurements was also checked.

Results

The headspace analysis on the vials, highlighted an evolution of the bell peppers volatilome during the shelf-life experiments. Despite the substantial inter-shipment variation observed in quality, notable trends in VOCs emissions emerged. First of all, a concentration decrease of most mass peaks was observed over time, including mass peaks associated with key bell peppers aroma compounds like *m/z* 101.096 and 137.134, tentatively identified as hexanal/(E)-2-hexen-1-ol and a mixture of monterpenes (ocimene, myrecene and limonene) [3-4]. This was correlated with other quality markers as weight loss and firmness (penetration test) which also decreased over time. Some differences between the BB and the standard way of storage were also observed for some mass peaks, especially as the shelf life progressed. For both *m/z* 33.034 and 47.049 (Figure 1) identified as methanol and ethanol the standard treatment showed higher concentrations both during storage at room (20°C) and refrigerated temperatures. These compounds are used as quality bio-markers since they can indicate microbial fermentation or spoilage resulting in the breakdown of sugars and other organic compounds.

By using O_2^+ as primary ion, ethylene emissions were measured during the respiration rates experiment where samples were incubated for 30 minutes at room temperature. In Figure 2, the trend of *m/z* 28.031 for peppers of the second shipment is shown. Ethylene emissions remined quite stable over time for peppers stored at 7°C with the exception of an increase observed after 20 days of storage. The average emission was significantly lower ($P. < 0.05$) for the peppers stored in the BB.

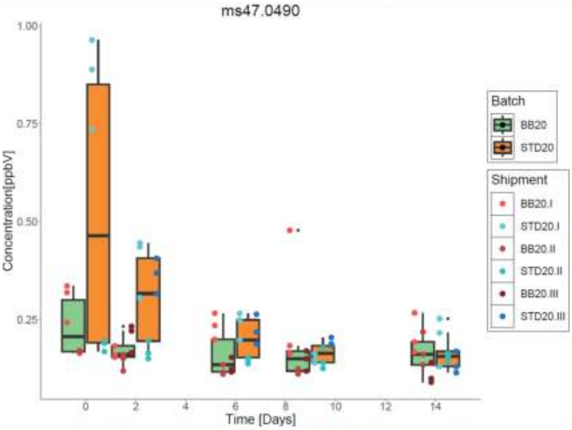

Figure 1: m/z 47.049 (Ethanol) trend during the shelf life of peppers at 20°C. The color of the points represents the different shipments for the two different treatments.

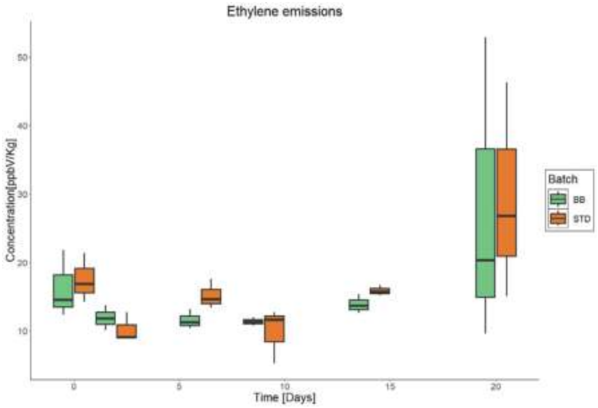

Figure 2: m/z 28.036 (Ethylene) trend during the shelf life of peppers of the second shipment stored at 7°C. The concentration is normalized by the samples weight.

Discussion & conclusions

The BB developed inside the SISTERS project showed promising results for better preserving bell peppers quality during the post-harvest phases of transportation and storage. PTR-ToF-MS was successfully applied to monitor respiration rates and VOCs emissions during the shelf life of bell peppers (*cv* Lamuyo). The technique, not only allowed to follow changes of some important quality markers over time, but was also successfully applied to measure ethylene emissions by using O_2^+ as primary ion. Ethylene is a crucial biomarker in the postharvest management of peppers, playing a pivotal role in signaling and regulating various physiological processes that directly influence the quality, ripening, and freshness. While the correlation between PTR VOCs profiling and other instrumental and sensory data requires further exploration, these initial findings underscore PTR-MS as a valuable tool for rapid and broad evaluation of the post-harvest quality of green Lamuyo peppers. The technique was also used to validate the BB performance which depends on the physiological characteristics of the fresh products, including respiration rates.

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Neighborhood-level inequality in Hazardous Air Pollutant emissions measured over Los Angeles

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Abstract

In the United States, $PM_{2.5}$ and NO_x pollution disproportionately burden communities of color and of lower income [1,2]. However, such information is lacking when it comes to hazardous volatile organic compounds (VOCs), for which city-wide measurements are more challenging and thus are mostly not available in routine observations.

Here we use spatially resolved airborne measurements of VOC concentrations and emissions performed in the Los Angeles basin during daytime in June 2021, and combine them with census tract-level census information. We find that the concentrations of the observed hazardous air pollutants – for example, benzene, naphthalene, and *p*-chlorobenzotrifluoride – are higher in neighborhoods with lower incomes and with a higher percentage of Hispanic and Latino population. The mixing ratios of some of the hazardous air pollutants are 40% higher for low-income Hispanics and Latinos than for high-income non-Hispanic Whites. This inequality is even larger (up to ~70%) for emissions than for mixing ratios, demonstrating that disadvantaged communities live closer to the emission sources. Consequently, it can be expected that the inequality in mixing ratios will increase under stagnant meteorological conditions. Toluene/benzene emission ratios in combination with the demographics of the census tracts indicate that the above-described inequalities are caused mainly by non-traffic emission sources such as industry and solvents.

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ptairMS: processing and analysis of PTR-TOF-MS data for biomarker discovery in exhaled breath

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Abstract

The analysis of Volatile Organic Compound (VOCs) in exhaled breath is a non-invasive method for early diagnosis and therapeutic monitoring. Proton Transfer Reaction Time-Of-Flight Mass Spectrometry (PTR-TOF-MS) is of major interest for the real time analysis of VOCs and the discovery of new biomarkers. However, there is currently a lack of methods and software tools for handling PTR-TOF-MS data obtained from cohorts for biomarker discrovery in exhlaed breath.

We therefore developed a suite of algorithms that process raw data from several files and build the table of feature intensities in all samples, through 1) expiration and peak detection, 2) quantification, 3) alignment between samples 4) missing value imputation and 5) suggestion of feature annotation. Notably, we developed an innovative two dimensional peak deconvolution model based on penalized splines signal regression, as well as methods for the selection of the VOCs which are specific from exhaled breath and the correction of the ambient air baseline. The workflow is freely available as the ptairMS R/Bioconductor package. The package also includes a Shiny graphical interface to facilitate data management and analysis by the end-user.

Our approach was validated both on experimental data (mixture of VOCs at standardized concentrations) and simulations, which showed that identification of VOCs from exhaled air sensitivity reached 99%. Furthermore, application to clinical data from ventilated patients resulted in the detection of four biomarkers of COVID-19 infection. Altogether, these results highlight the value of the ptairMS approach for biomarker discovery in exhaled breath.

Quantification of Oxygenated Volatile Organic Compounds using Collision-Induced-Dissociation during the AEROMMA Campaign

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Abstract

A current bottleneck in accurately predicting the impacts of urban emissions on secondary pollution, including ozone and secondary organic aerosol, is the quantification of oxygenated volatile organic compounds (OVOCs). In this work, a voltage scanning (VS) method for quantifying OVOCs, utilizing collision-induced dissociation, is developed using the VOCUS chemical ionization mass spectrometer operated with ammonium as reagent ions. The method is optimized in laboratory studies and tested in the most challenging environment aboard a scientific aircraft during the AEROMMA 2023 campaign to quantify OVOCs in plumes over the Chicago metropolitan area. Voltage scans are optimized to produce for the first-time outcomes down to within a 5-second time resolution. Several OVOCs are quantified that originate from unconventional emerging pollution sources in urban air including cooking and daily household chemicals, in particular solvents and fragrances. Furthermore, the VS method is used to successfully quantify oxidation products within these emissions, notably organic nitrates, traditionally difficult to calibrate. Importantly, we determine the sensitivity of a prevalent organic nitrate in urban air, laying the foundation for refining chemical transport models. This study therefore demonstrates the voltage scanning method's versatility and effectiveness in quantifying complex compounds during field measurements, particularly in urban environments.

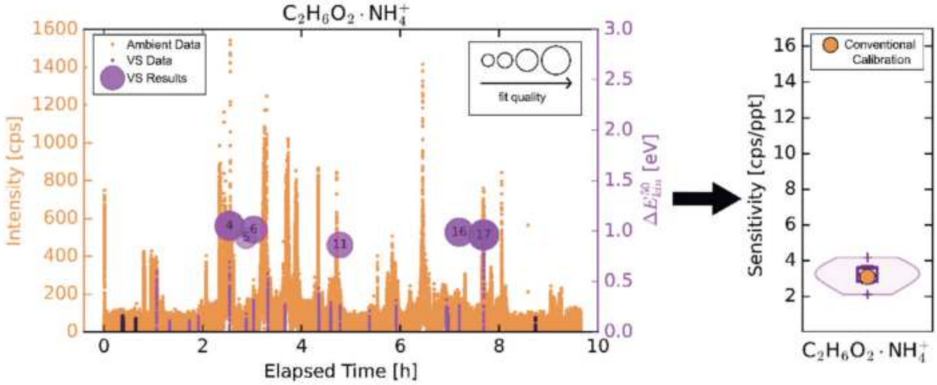

Figure 1: In the left time series of C6H6O2 ionized by NH4 +, the data points used for the VS (Voltage Scanning) fitting are indicated. The ΔE50kin results for the respective VS data section are displayed on the second y-axis. ΔE50kin is the kinetic energy of the cluster at half signal strength derived from a VS measurement, where an increase in electric field strength in a scanning region results in a reduction of signal due to collision induced dissociation. The size and opacity of the ΔE50kin markers are adjusted based on the r2 of the fit, with the number of the VS labeled in circles for easier identification. The Violin plot on the right illustrates the sensitivities corresponding to these ΔE50kin values together with the measured sensitivity to Ethylene Glycol in the lab (orange). In the violin plot, the median and values for the upper and lower quartiles are presented.

The Manual Pyeakfitter – a new interpretation of a helpful tool for interpreting mass spectra

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Abstract

The Manual Pyeakfitter [1] is a peak-fitting program designed for TOF-MS data preprocessed by the TOFTracer2 program [2]. Its primary purpose is to generate a suitable mass-list by hand for a given spectrum. The decision to add a specific mass or composition to the list is guided by a comparison of the spectrum with a best local fit. This functionality is implemented in a simply structured and easy-to-use interface. Python is chosen as the programming language due to its widespread use and the existence of the well-documented package for the QT framework (PYQT). The program is available on git hub with a CC BY-NC-SA 4.0 License [1].

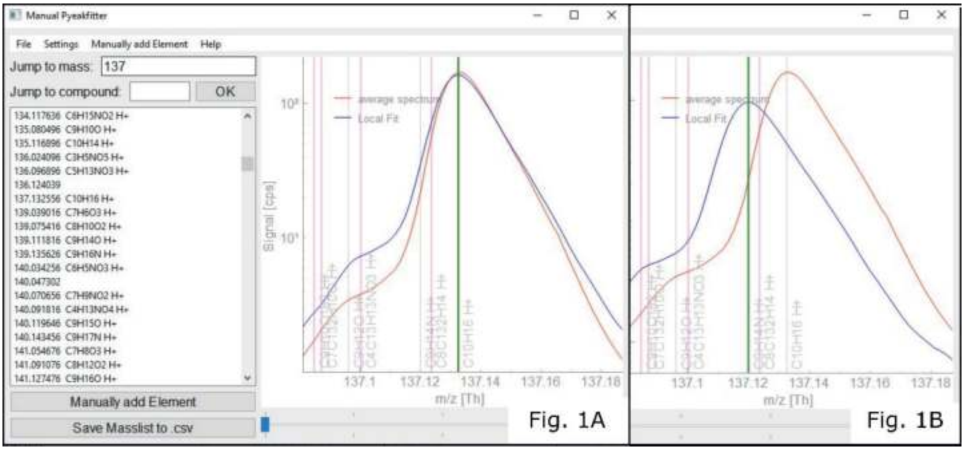
Introduction

One primary goal in analyzing high resolution mass spectra is to determine which chemical sum formulae correspond to the peaks in the spectrum. This is particularly crucial in cases where the chemical composition of the analyte gas is initially unknown, such as in the analysis of outside air or oxidation products of complex chemical systems, as done in the CLOUD experiment at CERN. After calibrating the mass axis with peaks at known masses, unidentified peaks can be identified by comparing their position on the mass axis with the exact mass of potential sum formulae. If the user determines that a compound is represented in the spectrum, the mass and sum formulae are added to the mass-list for further processing. This process of analyzing the mass spectrum and identifying peaks is facilitated by the newly developed Manual Pyeakfitter program, which is an advancement of the Manual Peakfitter program [3]. The main goals of rewriting this program were:

- Ability to add new elements, such as sulfur, or new isotopes like O(18)
- Using the Python programming language instead of C++, which is easily understood by many users and makes the program more flexible and adaptable to new requirements
- Implementation of new interactive graphical user interface (GUI) features and quality-of-life improvements.

The Manual Pyeakfitter

The program is constructed in the PYQT [4] framework, which is a Python implementation of the QT framework, responsible for handling the interaction with the operating system and building the GUI. For plotting, the PYQTgraph package [5] is utilized. It is faster than the standard Matplotlib plotting package and integrates well into the PYQT framework. Figure 1A illustrates a typical view of the program, where on the left, all the masses, already present in the mass-list, are displayed, and on the right, a segment of the average spectrum is shown. For each peak, the program generates multiple suggestions of sum formulae, represented in grey, and created through different combinations of common elements. The pink lines represent the masses of isotopes of lower masses in the mass-list. As of now, the contributions of C(13) and O(18) isotopes are implemented, but the adjustable code of the manual pyeakfitter makes the implementation of more isotopes straightforward. In Figure 1A, the sum formula of $C_{10}H_{16}H^+$ is selected, where the local fit aligns well with the spectrum. Conversely, in Figure 1B, it is evident that the local fit for $C_9H_{14}NH^+$ does not match well. The local fit is generated by a linear combination of single peaks, weighted by coefficients determined through solving a least squares problem.



Jump to mass: 137

Jump to compound:

```
134.117636  C6H15NO2 H+
135.080496  C9H10O H+
135.116896  C10H14 H+
136.024096  C3H5NO5 H+
136.096896  C5H13NO3 H+
136.124039
137.132556  C10H16 H+
139.039016  C7H6O3 H+
139.075416  C8H10O2 H+
139.111816  C9H14O H+
139.135626  C9H16N H+
140.034256  C6H5NO3 H+
140.047302
140.070656  C7H9NO2 H+
140.091816  C4H13NO4 H+
140.119646  C9H15O H+
140.143456  C9H17N H+
141.054676  C7H8O3 H+
141.091076  C8H12O2 H+
141.127476  C9H16O H+
```

Figure 1: A typical view of the manual pyeakfitter program. In figure A the selected sum formula results in a local fit aligning well with the spectrum, whereas in figure B the local fit does not match well. This is how the manual pyeakfitter can aid the user interpreting mass spectra

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Real-time monitoring of permeation processes in polymer films using a micro-chamber/thermal extractor coupled to PTR-TOFMS

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Abstract

Plastic packaging materials act as functional barriers to preserve the packaged product from external contaminants. Lag time experiments can be performed to characterize the barrier properties of polymer films. Although an established method based on gas chromatography-flame ionization detection (GC-FID) exists for determining and predicting lag times, it is laborious and not suitable for investigating rapid permeation processes. The present study aimed to develop a real-time monitoring approach to characterize film barrier properties using proton transfer reaction time-of-flight mass spectrometry (PTR-TOFMS) to allow for the investigation of fast permeation processes of volatile organic compounds (VOCs) through polymer films. A PTR-TOFMS was coupled to a commercial micro-chamber/thermal extractor (μCTE) device incorporating a bespoke permeation insert to allow for the migration of 2,3-butanedione as a selected target compound through a high-density polyethylene (HDPE) film at 40 °C. The compound broke through the barrier at detectable concentrations after about 100 min and reached a plateau after 450 min. The results showed that this novel approach is capable of monitoring the permeation rate in real-time so that, in a prospective step, the empirical data can be used to calculate lag times to determine the barrier properties of packaging films.

Introduction

Packaging applications represent the largest sector of the European plastic material demand, with approximately 19.7 Mt of polymer material used for plastic packaging in 2021 [1]. Usage is dominated by polypropylene (PP), polyethylene (PE) or polyethylene terephthalate (PET) [2]. The purpose of using packaging is to protect the packaged product inside. Besides preventing the product components from leaking, plastic packaging materials act as a barrier to protect the packaged goods from unwanted compounds that could migrate into the product from external sources [3]. Adequate packaging prevents food from contamination and spoilage, thereby increasing its shelf life and helping to reduce food loss and waste [4-6]. The main parameter influencing the barrier properties of packaging materials is the distribution equilibria (diffusion constant) between the donor phase and the barrier material. One possible method to determine this material-specific parameter is to perform lag time experiments [3]. Ewender and Welle [7] developed an automated method to determine lag times of polymer films and investigated the permeation of hydrocarbons through high-barrier polymer films at temperatures between 70 °C and 120 °C, subsequently using a diffusion model to predict lag times at ambient temperatures. The migrated compounds were analyzed by gas chromatography with flame ionization detection (GC-

FID), with data acquisition every 40 min [7]. The latter is a limiting factor for fast permeation processes, when the number of acquired data points are too low for extrapolation. The objective of the current work was to develop a method to investigate permeation processes using proton transfer reaction time-of-flight mass spectrometry (PTR-TOFMS) for online analysis of target volatiles. The intended outcome of this novel approach is to establish a method for real-time monitoring of permeation that is capable of analyzing fast permeation processes of individual volatile organic compounds (VOCs) at ambient temperatures. In terms of investigating barrier functions of packaging materials, this can potentially broaden the range of analyzed compounds and material characteristics and act as a basis for the development of fast screening methods.

Experimental Methods

A 500 μm high-density polyethylene (HDPE) TIPELIN 6000B polymer film was used as a representative barrier material. The sampling was carried out using a commercial micro-chamber/thermal extractor™ (μCTE) system and a compatible permeation insert (both MARKES International, Bridgend, UK). The μCTE was held at a constant temperature of 40 °C and the permeation insert was placed in the μCTE for preheating. A sealed vial containing 2,3-butanedione (CAS 431-03-8, ≥ 99 % purity, Fluka, Steinheim, Germany) was equilibrated at 40 °C to create a saturated headspace sample. For the measurements, the polymer film was clamped in the permeation insert. Then, 100 μL of saturated 2,3-butanedione headspace was injected in the chamber below the test material, after which the permeation insert was placed in the μCTE. The μCTE was constantly flushed with filtered, pressurized air to purge the gas above the polymer film (containing the VOCs migrating through the film) into the PTR-TOFMS instrument (PTR-TOF 8000, IONICON Analytik GmbH, Innsbruck, Austria) for continuous analysis. The μCTE and the PTR-TOFMS instrument were coupled via a custom-built adapter, developed in a previous work and reported by Pham *et al*. [8]. The PTR-TOFMS was operated at a TOF pressure of 10^{-6} mbar and a TOFLens pressure of 10^{-7} mbar. The drift tube was set to 555 V, 2.2 mbar, and 60 °C, resulting in a reduced electric field (*E/N*) of 105 Td. The signal intensities of 2,3-butanedione (*m/z* 87.044) were acquired for 500 min after the injection with a data acquisition rate of 0.1 Hz, respectively; analyses were performed in duplicate. The normalized counts per seconds (ncps) were calculated by transmission-correction and normalization to the H_3O^+ primary ion signal (*m/z* 21.022; multiplier = 500). A standard reaction rate coefficient of $k = 2\times10^{-9}$ cm^3s^{-1} was assumed.

Results and Discussion

The permeation kinetics of 2,3-butanedione through the polymer film are shown in Fig. 1. The signal intensity of *m/z* 87.044 was observed to increase about 100 min after injection of the compound into the μCTE. After 450 min, *m/z* 87.044 reached a plateau, indicating a constant permeation rate.

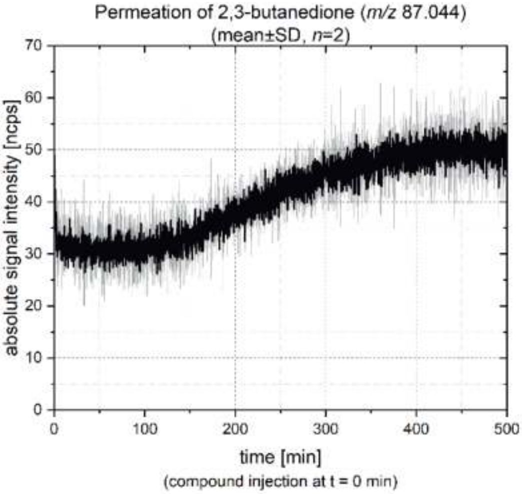

Figure 1: Permeation of 2,3-butanedione (m/z 87.044) through a 500 µm HDPE film at 40 °C.

One important prerequisite for the success of lag time experiments is a constant concentration of the analyzed permeant in the donor phase [3]. On the one hand, especially in small volumes with low permeant concentration, a depletion could occur and affect the permeation rate before reaching a constant level. On the other hand, a concentration of the permeant that is too high could cause a swelling of the polymer and, consequently, impact the diffusion constant [7]. In this study, 100 µL of saturated headspace sample were injected in a sampling chamber with a volume of about 4 mL. Hence, the 2,3-butanedione concentration was about a factor of 40 below saturation. The stability of the signal after reaching the maximum intensity provides a proof-of-concept that the lag time can be derived from such online PTR-TOFMS data. The aim for future experiments is to validate the capability of this approach by investigating the permeation process for different polymer films and a variety of VOCs with distinct characteristics (e.g., volatility and polarity); this would allow for subsequent comparison with established methods for evaluating barrier functions. Ultimately, sampling the permeants on sorbent tubes followed by an off-line analysis via thermal desorption combined with comprehensive two-dimensional GC (GC×GC)-TOFMS can act as a complementary approach to support compound identification. This can be advantageous, especially for the analysis of permeation processes with complex and unknown composition rather than defined standard compounds [9].

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Next-Gen PTR-TOFMS Mass Resolution: Worth It?

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Abstract

Common high-resolution Proton-Transfer-Reaction Time-Of-Flight Mass Spectrometry (PTR-TOFMS) instruments offer mass resolutions between 5,000 and 7,000 m/Δm (Full-Width-Half-Maximum; FWHM). Recently, Next-Gen PTR-TOFMS devices have been introduced with mass resolutions up to 15,000 m/Δm. This development raises the question, if such an extreme boost in resolution is rather just an impressive number in the instrument's spec sheet or if it comes with real, game-changing benefits for everyday analyses.

Here, the answer is given in form of direct comparisons between common and Next-Gen resolution data obtained from the analysis of food samples (head-, mouth- and nosespace) and the outcome is unambiguous. For complex matrices, up to 15,000 m/Δm mass resolution opens completely new insights into the chemical composition of samples and enables clear separation of previously indistinguishable isobaric compounds.

Introduction

The story of mass resolution in PTR-MS has always been an interesting one. Decades ago, when quadrupole mass filters with nominal mass resolution were state of the art, the scientific world seemed to be quite straight-forward. When reading publications from this aera one could get the impression, that a detected ion signal at a nominal *m/z* could be rather unambiguously assigned to a specific compound. However, this dramatically changed upon the introduction of PTR-TOFMS, where it became clear that there is a multitude of different isobars present at virtually every nominal *m/z* [1]. Nowadays, mass resolutions between 5,000 and 7,000 m/Δm are considered "high resolution", particularly given the rather low *m/z* of common VOCs (up to about *m/z* 300).

Here, we want to answer the question, if boosting this resolution by a factor of 2-3, i.e. to about 15,000 m/Δm, will give a substantial benefit for real-world analysis. We present data from a Next-Gen IONICON PTR-TOFMS device during the analysis of chocolate and other complex food matrices and compare these data to downsampled 5,000 m/Δm spectra.

Experimental Methods

The utilized instrument for the present study was a PTR-TOF 10k [2]. These devices are equipped with the ioniTOF 10k mass analyzer which can achieve mass resolutions between 10,000 and 15,000 m/Δm. Recently, the ioniTOF 10k was thoroughly characterized by Reinecke et al. [3] in a different Next-Gen PTR-TOFMS model, namely a FUSION PTR-TOF 10k. The two devices differ mainly in their PTR part. That is, while the reaction region of the PTR-TOF 10k consists of the conventional combination of a DC drift tube followed by a DC+RF ion funnel, FUSION depicts a revolutionary new DC+RF PTR reaction region design (for details see [3]).

An exemplary determination of the actual mass resolution is shown in Figure 1. Limonene was introduced into the instrument's sampling line until a good signal-to-noise ratio was reached, but the signal intensity was still far from showing any saturation effects. Subsequently, the signal maximum was normalized to 1 and the peak width Δm was measured to be *m/z* 0.009 at a signal height of 0.5 (i.e. FWHM). This results in a mass resolution of 15,055 m/Δm.

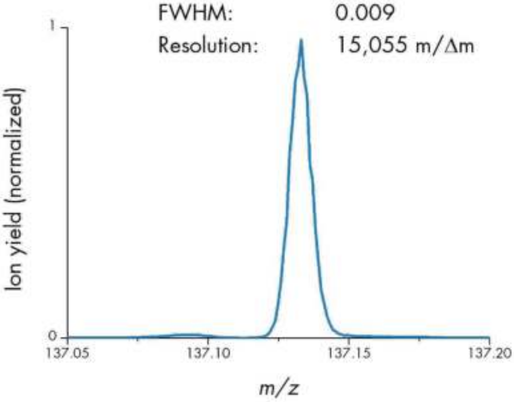

Figure 1: Part of a mass spectrum recorded with the PTR-TOF 10k showing the protonated limonene peak (maximum normalized to 1).

Sample materials used for the present study were common food products, in particular different flavors and brands of chocolate, purchased from a local supermarket. Food samples were chosen because of their complex matrices comprising a plethora of (isobaric) VOCs, especially when analyzed in human mouth- and nosespace after consumption (e.g. [4]).

Results and Discussion

Already at a first look at the mass spectrum around *m/z* 147 of exhaled breath after the consumption of caramel chocolate, the benefits of about 15,000 m/Δm get obvious because of the great details revealed (Figure 2; screenshot from PTR-MS Viewer 3.4 [5]). For the sake of simplicity only the clearly separable peaks were defined in the software and the maximum heights as well as the center positions were transferred to a purpose-built peak simulation program. Figure 3 shows the reproduced peakshapes from these data for 5,000 and 15,000 m/Δm. At 5,000 m/Δm basically only one peak at about m/z 147.08 is clearly identifiable, with a shoulder on the left and a shoulder on the right slope. Additionally, below m/z 147.00 there is a broadened structure presumably containing more than one peak. At 15,000 m/Δm nine peaks are perfectly separated and, more even importantly, six peaks can be tentatively assigned to compounds relevant in food and flavor analysis (calculated chemical formulae in the Figure).

That is, in this case the increased mass resolution of the PTR-TOF 10k is crucial for a selective analysis, while with common 5,000 m/Δm devices only an unspecific sum of isobars could be detected and quantified.

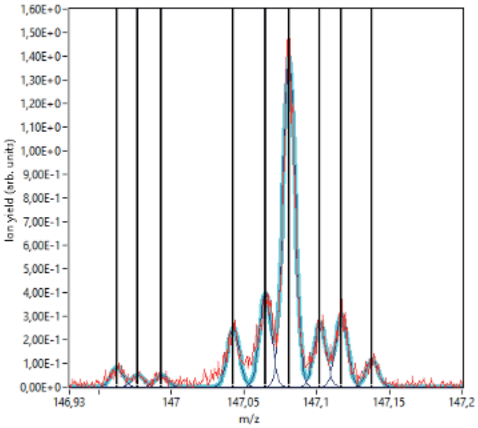

Figure 2: Mass spectrum (red) around m/z 147 of exhaled breath after the consumption of caramel chocolate; clearly separable peaks defined with centers (black vertical lines), Gauss fits (blue) and sum of fits (turquois).

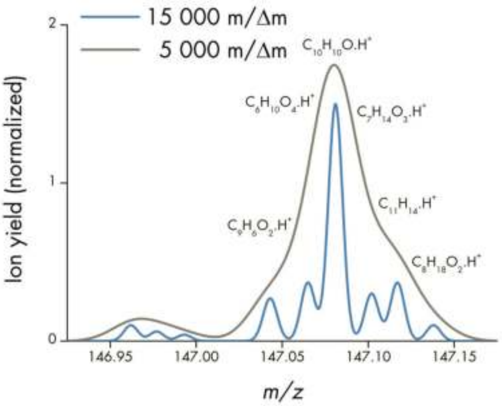

Figure 3: Data from Figure 2 reproduced with Gauss curves at the actual 15,000 m/Δm (blue) and downsampled to 5,000 m/Δm (grey) for direct comparison; compounds relevant for food and flavor research tentatively identified via exact m/z and isotope ratios.

In order to demonstrate the importance of being able to quantify the isobars separately, we selected two compounds tentatively identified as $C_{10}H_{10}O$ and $C_7H_{14}O_3$ and compared their intensities in nosespace air during the consumption of caramel chocolate from two different manufacturers (A and B). In Figure 4 first a baseline is established by three exhalations through the nose from about 0 to 50 s. Subsequently, a piece of caramel chocolate from manufacturer A is put in the test subject's mouth and a steady increase of the $C_7H_{14}O_3$ signal is visible, while the chocolate slowly melts, reaching a maximum around 200 s, which is when the chocolate was fully swallowed. $C_{10}H_{10}O$

follows a similar trend, however, at about one order of magnitude lower intesities. For caramel chocolate from manufacturer B the situation is quite different. Here, $C_7H_{14}O_3$ remains at the baseline level throughout the whole consumption process, while $C_{10}H_{10}O$ is not only somewhat higher in intensity, but also released over a considerably longer time than in sample A.

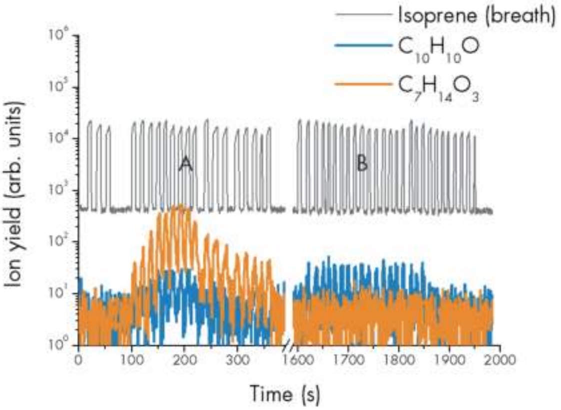

Figure 4: Ion yield vs time diagram for three selected compounds in nosespace (isoprene signal indicates exhalations); first three exhalations are blank breath, followed by consumption of caramel chocolate from manufacturers A and B.

Based on this straight-forward example it can already be concluded that the extremely high mass resolution of the ioniTOF 10k (utilized in PTR-TOF 10k and FUSION PTR-TOF 10k) is of indisputable advantage for the analysis of complex matrices.

We will show a series of further food and flavor analysis experiments which support this conclusion.

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Insight into spatial variability upon the O_3-precursor relationship in a city of the North China Plain

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Abstract

A five-month field campaign was conducted in the summer of 2019 to investigate the ozone (O_3) formation chemistry through multiple-site and continuous observations in a major prefecture-level city of northern China, based on box modeling (MCMv3.3.1) and somg production model (SPM). Based on moer comprehensive dataset from three observational sties, the good agreement for quantification of O_3 formation chemistry was showed between box model and SPM[1]. In this city, the high-O_3 polluted areas dominantly distributed in the central and northern regions, while low-O_3 polluted areas mainly located at the southern region. Indicated by various geostatistical methods, the spatial characteristics of O_3 precursors showed significant differences in this city, which also obviously affected the spatial pattern of O_3-precursor relationship. Meanwhile, the southern and northern regions were mainly characterized as high-extent (E(*t*)) agglomeration, while the central areas presented with low-E(*t*) agglomeration. Compared with low-O_3 hours, the spatial O_3-VOC-NO_x sensitivity was inclined to be significantly non-aggregation during the polluted period, which challenged the local O_3 precise prevention at the spatial scale of this city to some extent. During high-O_3 hours, the high E(*t*) diurnal variation primarily found in the northern region, while the low E(*t*) mainly observed in the central area, implying that the northern diurnal variations of the extent for O_3 formation chemistry were stronger, which may be driven by the spatial variability of O_3 precursors in this city. During high-O_3 hours, the photochemical regimes were mainly considered as transitional (in the central region) and NO_x-limited (in the southern and northern region) in this City. Therefore, the central region in this city should emphasize the importance of synergistic reduction of NO_x and VOC, while the southern and northern regions should focus on NO_x reduction. Along with the NO_x-O_3 sensitivity gradually enhanced at the spatial scale, the summertime O_3 pollution significantly and correspondingly increased in this city. Hence, when the O_3 pollution is found in the growth stage in this city, more endeavor should focus on synergistic reduction especially for NO_x emission to alleviate the growth process of O_3 pollution.

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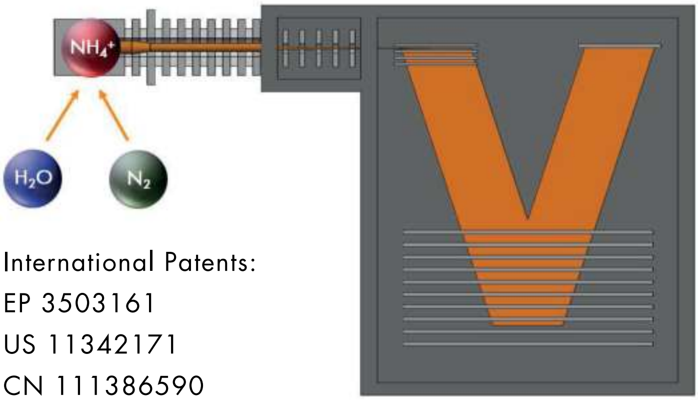
NH_4^+
H_2O
N_2

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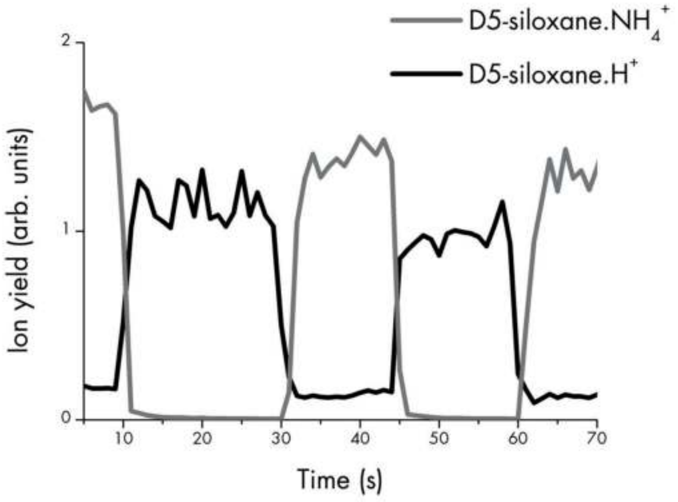

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