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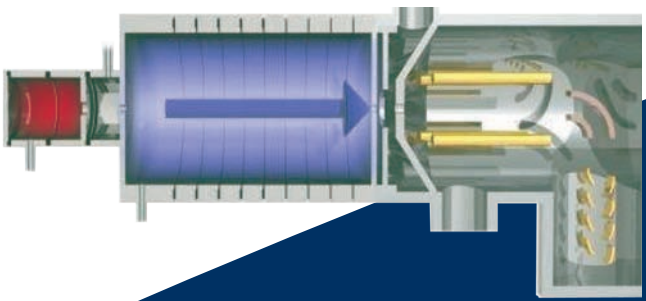

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Jürgen Dunkl
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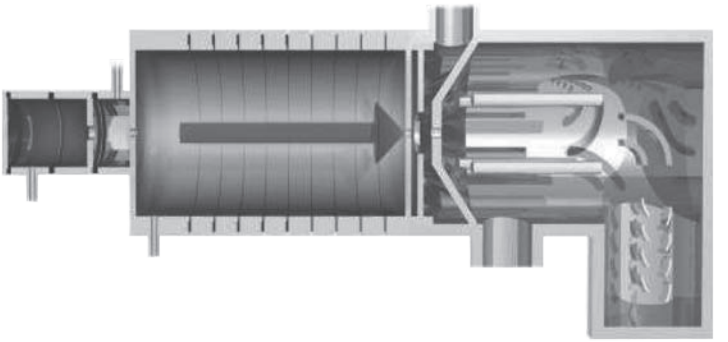

Contributions

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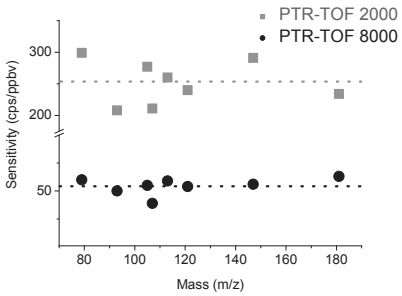

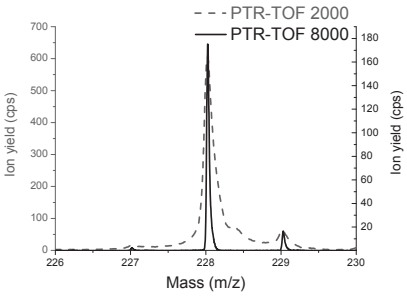

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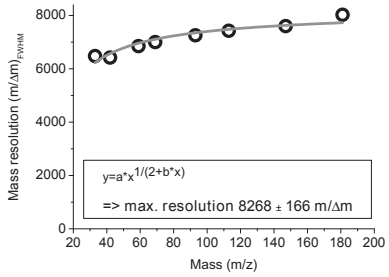

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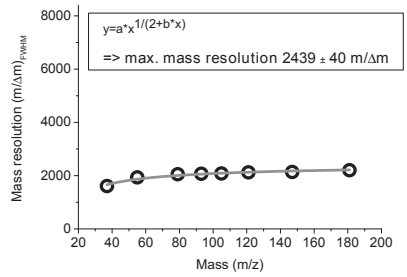

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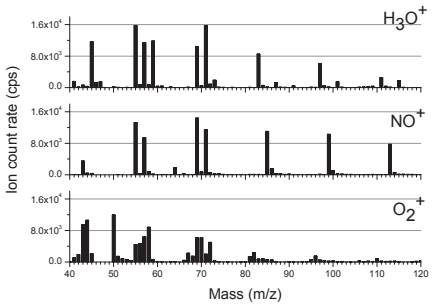

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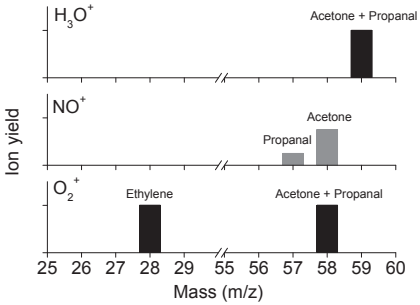
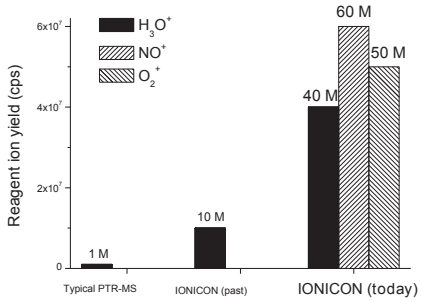


■ Identification of isomeric compounds



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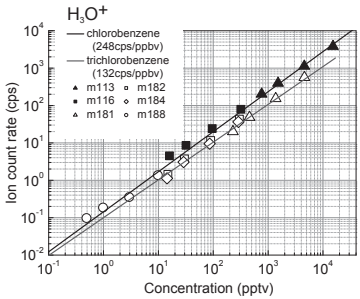

■ Improved sensitivity and detection limit

Sources:

R. S. Blake et al. Chem. Rev., 109 (3) (2009), 861-896.
A. Jordan et al. International Journal of Mass Spectrometry (2009), 32-38.

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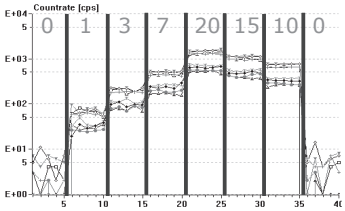

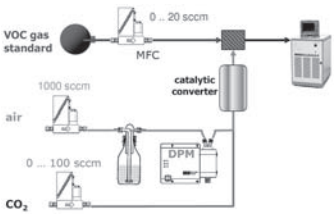

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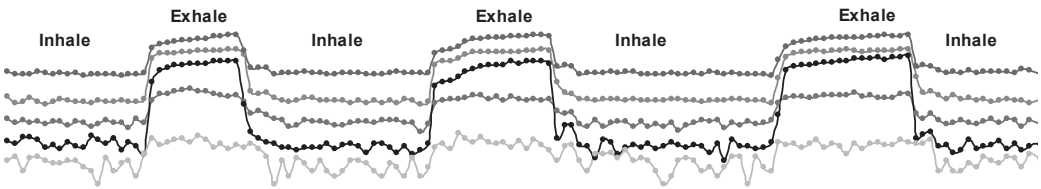

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Foreword

PTR-MS (Proton Transfer Reaction - Mass Spectrometry) is a technology developed at the Institute of Ion Physics and Applied Physics at the University of Innsbruck in the 1990's. PTR-MS has been found to be an extremely powerful and promising technology for the online detection of volatile organic compounds (VOCs) at trace levels (pptv) in gaseous media. PTR-MS has been successfully employed in many fields of research including environmental research, life sciences, and food & flavor technology.

More than ten years ago the spin-off company Ionicon Analytik GmbH (www.ptrms.com) was founded to provide PTR-MS instruments to a growing user community and to develop the technology further. In 2004 Ionimed Analytik GmbH (www.ionimed.com) was founded to provide trace gas solutions for the fields of biotechnology and medicine. Today more than 150 research institutions and companies throughout the world use this technology.

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 VOCs. The 5th PTR-MS conference continues this biennial series to provide a discussion forum for PTR-MS users and scientists from both academia and industry. More than 115 conference participants are expected at the conference site in Obergurgl. This year's conference is organized in plenary sessions and focused parallel sessions. The program will start with a plenary session with key note speakers presenting interdisciplinary overviews in environmental science, food science and medicine. On the following three days the conference topics PTR-MS in Environmental Science, Food Science, Medicine & Biotechnology, PTR-MS technology and Safety & Security will be discussed in parallel sessions.

I would like to thank the session chairs Saskia van Ruth & Franco Biasioli (Food Science), Jens Herbig (Medicine and Biotechnology) and Philipp Sulzer & Tilmann Märk (Detection and Monitoring for Safety, Security and Industry) for putting together an exciting programme which exemplifies the growing number of PTR-MS applications in various scientific disciplines.

Special thanks go to Jürgen Dunkl, Martin Breitenlechner and Sandra Naschberger who worked very hard to organise this conference. Finally I would like to thank the UNIVERSITY of INNSBRUCK, IONICON ANALYTIK, IONIMED ANALYTIK and the EUROPEAN COMMISSION for support. IONICON ANALYTIK also sponsors the poster award which will be bestowed to the three most impressive and innovative posters presented at the conference.

Armin Hansel

Innsbruck, January 2011

Applications in Medicine and Biotechnology

Exhaled breath analysis: a tour d'horizon

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Abstract

Volatile compounds released through exhaled breath, the nasal cavity, oral cavity, urine or sweat play an important role in the human metabolism. During the last decade the analytical instrumentation for detection of such compounds and determination of their concentrations has been considerably improved or even newly developed. Typical techniques used are gas chromatography with mass spectrometric detection (GCMS) and proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF).

A particular focus of exhaled breath analysis are *real-time* measurements, even down to breath-to-breath resolution. This makes it possible to detect very fast changes in concentrations of volatile compounds in exhaled breath. A typical example is isoprene, a hydrocarbon, which may change its concentrations in exhaled breath fast, e.g., during a challenge at the ergometer or during movements of legs, arms or head during sleep.

Analysis of exhaled breath for lung cancer patients is another focus, with a number of very interesting pilot results. Nevertheless this is still far from a clinical test, for which it would be necessary to compare not only lung cancer patients to healthy volunteers, but also to patients suffering from other lung diseases such as chronic obstructive pulmonary disease (COPD).

Introduction

Volatile compounds released through exhaled breath, the nasal cavity, oral cavity, urine or sweat play an important role in the human metabolism. Different techniques for gas analysis have been developed and used for analysis of exhaled breath:

- gas-chromatography with mass spectrometric detection (GCMS)
- proton-transfer-reaction mass spectrometry (PTR-MS)
- laser spectrometry
- ion mobility spectrometry and
- sensors or sensor arrays.

Volatiles in breath or from the nasal and oral cavities can be sampled as often as it is desirable and may serve as probes for biochemical changes in the body. Particularly promising are *real-time* measurements even down to breath-to-breath resolution. This allows detection of fast changes in concentration as observed, for example, for nitric oxide in the nasal cavity or of isoprene in breath. Nitric oxide appears in almost every organ of the body and has a bactericidal

effect in the nasal cavity and the sinuses. Isoprene is a by-product of cholesterol biosynthesis and observed in exhaled breath in relatively high concentrations of ~100ppb.

Experimental Methods

The methods used for the results shown here are

- proton-transfer-reaction mass spectrometry (PTR-MS),
- gas chromatography with mass spectrometric detection (GC-MS) with solid phase microextraction (SPME),

The PTR-MS was a high-sensitivity instrument. The solid-phase microextraction (SPME) coupled to GC-MS had a limit of detection of ~2ppb (depending on the particular compound in question).

Results

Fig 1 shows an exemplary result of *real-time* measurement for isoprene [nmol/Lit/min], acetone [a.u.] and CO_2 [Lit/min]. This refers to a healthy volunteer on an ergometer, under a workload of 75 W (three different phases with intermediate recovery). At the start of each workload phase, isoprene shows a huge increase in concentration whereas acetone output is in agreement with the CO_2 output. This indicates that isoprene is stored in the body and released under certain conditions [1,2]. It also shows that concentrations of *certain* compounds in exhaled breath may change fast under workload.

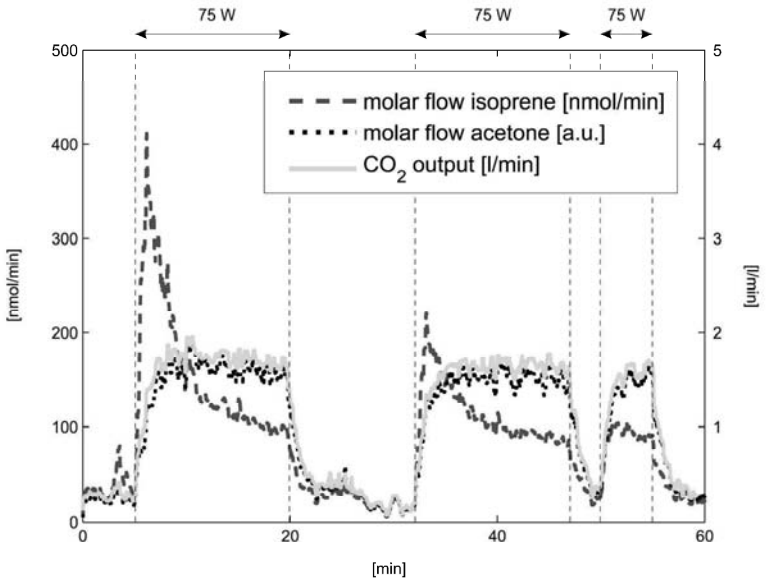

Figure 1: Example of a real-time measurement of exhaled breath for a volunteer on an ergometer, with workload of 75 W and recovery phases. For detailed information see references 1 and 2.

A particularly interesting field is the analysis of exhaled breath for lung cancer patients. Some results using GCMS with solid phase microextraction (SPME) are shown in Fig 2 [3]. These results refer to lung cancer patients (CA) and healthy volunteers. On the x-axis, the different compounds (isoprene, acetone, acetonitrile, etc) are listed. On the y-axis the patients and volunteers are listed according to their smoking habits. The concentrations of the listed compounds in exhaled breath are given in a colorcode (LOD of the compounds being around 2 ppb in the present SPME measurements). Some compounds such as isoprene and acetone appear in everybody's breath, other compounds like acetonitrile are related to smoking. Still other compounds appear primarily in the exhaled breath of cancer patients and are singled out by white vertical lines.

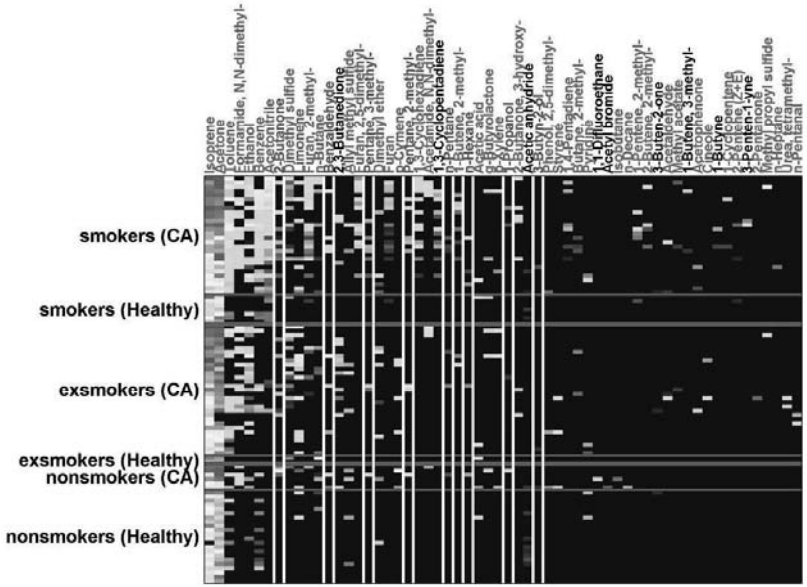

Figure 2: Comparison of the concentration profiles of lung cancer patients (CA) and healthy volunteers, listed according to their smoking habits. For detailed informations see reference 3.

Discussion

Research in volatile compounds is still in its infancy. For example, the proper sampling of exhaled breath or the influence of indoor air contaminations are still a matter of debate [4]. Furthermore the biochemical background of many volatile compounds is unknown.

Additional biochemical information could be achieved through investigation of volatiles released from cell cultures [5]. Particularly promising are experiments and breath tests using isotopically labelled precursors.

Some breath tests relying on ^{13}C-labelled precursors are already in clinical practice. Among them is the ^{13}C-urea breath test for infection with Helicobacter pylori. This opens a new area of non-invasive *personalized* medical diagnostics and therapeutic monitoring.

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Implementation of PTR-MS as tool in bioprocess monitoring – measurement of volatile components in the bioreactor exhaust gas

Gerald Striedner[1,2], Markus Luchner[1,2], Rene Gutmann[2,3], Armin Hansel[3], Karl Bayer[1,2]

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[2] *ACIB - Austrian Centre of Industrial Biotechnology*

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Abstract

Common bioprocess conditions imply a gas-liquid-mixture with living cells as solid phase in a sterile environment which demands a great deal on sensor/analyzer technology and design. On-line access to physiology relevant process variables, the ultimate request of process engineers, is still very limited as complexity of biological systems additionally constrains direct measurements.

Living cells can be described as a closed compartment in the bioprocess and information on physiology only can be gained by measuring the cell compartment and its components or by detection of molecules in the gas/liquid phase. Quantification of intracellular components definitely yielding the highest level of physiology related information is not possible via direct on-line measurement. Molecules in the gas/liquid phase either provided by medium and gas input or emitted by cells (exa-metabolome) represent a class of analytes better suited for on-line monitoring. Within these analytes a series of volatile organic compounds (**VOC**s) is expected which is easy accessible via analysis of the fermenter exhaust gas.

The required high sensitivity for VOC measurements and a linearity range of multiple orders of magnitude are perfectly matched by the PTR-MS technology. For implementation of PTR-MS technology into bio process monitoring recombinant protein production processes with E. coli were used as model system. In first experiments around 40 VOCs were detected and 15 to 20 of them showing significant changes during the course of the process. Due to a limited mass resolution explicit assignment of masses to substances was not always possible and additional measurements with a PTR-TOFMS were required.

For some of the identified components a direct connection to host physiology is obvious but there are also unexpected molecules in the fermenter off-gas containing new maybe very valuable process information. The next steps will focus on detailed evaluation of the information content of PTR-MS data and how this information can be used in bioprocessing. Furthermore reproducibility of measurements and systems robustness will be tested.

From pharmacokinetics to sensory science: the versatility of PTR-MS in a multidisciplinary environment

Jonathan Beauchamp[1] and Andrea Buettner[1,2]

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[2] *Department of Chemistry and Pharmacy, Emil Fischer Center, University of Erlangen-Nuremberg, Erlangen, Germany*

Abstract

Since its development in the mid-1990s, PTR-MS has proven to be a powerful analytical tool in numerous disciplines, from environmental chemistry and food science to biotechnology and medicine, to name just a few. In some instances, different scientific endeavours can benefit from a common investigative approach. Such is the case for breath gas analysis, which has its uses in fields as diverse as medical science and food research. Within this context, PTR-MS may be considered a multidisciplinary tool. This paper details applications of PTR-MS for *in vivo* measurements and highlights the commonality of each approach despite their different goals.

Introduction

When PTR-MS was introduced to the scientific community in the early publications of the mid-to-late 1990s, the inventors had foresight in considering its enormous potential in diverse disciplines, with examples of its implementation in medical applications, food control and environmental research [1,2]. Today, PTR-MS is an established research tool in many scientific fields, as is evident by the assortment of contributions to the biennial PTR-MS Conference.

The utility of PTR-MS for *in vivo* analysis of volatile compounds is particularly relevant in medical science. It has been applied to manifold investigations including the study of cancer biomarkers [3], establishing and monitoring the status of anaesthesia [4], and assessing general endogenous compounds in healthy subjects [5], amongst others.

Regardless of the specific scientific field utilising breath gas or *in vivo* analysis, each benefits from certain characteristics of the PTR-MS method, most specifically its high temporal resolution, low detection limit, and insensitivity to water vapour in the sample gas. The investigations outlined in this paper exemplify applications of PTR-MS for *in vivo* investigations in several fields, whereby an interrelation between each is apparent.

Pharmacokinetics

The field of pharmacokinetics deals with investigating the uptake and distribution within the body of exogenous compounds. This may include the ingestion of dietary supplements or the uptake of externally exposed substances. Both of these issues are dealt with here.

Dietary supplementation

The distribution and efficacy of pharmaceutical drugs or dietary supplements are of great interest to pharmacists, medics and dieticians alike. We investigated the release into the breath of eucalyptol (1,8-cineole) after ingestion of a eucalyptol-containing capsule. We found that the time

at which this compound first appeared in exhaled breath after capsule ingestion had great inter and intra-subject variability (see fig. 1).

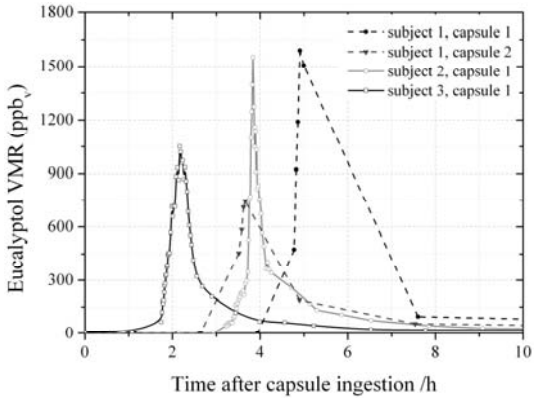

Figure 1: Breath release profiles of eucalyptol after capsule ingestion.

Furthermore, maximum eucalyptol concentrations were equally diverse. These phenomena could not be correlated to general physiology (e.g. body mass index) and were not sex-specific, but may have been partly due to state of satiety (which requires further investigation). Moreover, an important finding in these investigations was the transience of the peak, leading to repercussions for pharmacokinetic studies of traditional substrates such as blood, whereby analyses cannot be conducted as frequently and may lead to an oversight of such very brief peaks. This is discussed more extensively in the literature [6].

Toxicokinetics of environmental exposure

Environmental exposure to airborne compounds is not only of great relevance to health, but can also pose a problem for breath gas analysis by affording a background concentration in exhaled breath of exposure compounds that may be erroneously interpreted as endogenous markers.

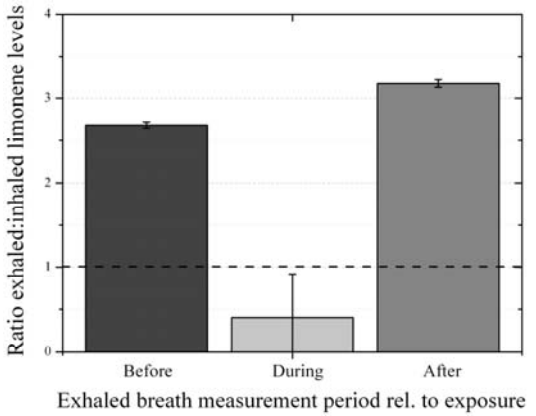

Figure 2: Ratio of exhaled:inhaled limonene in exhaled breath after 5 h exposure to 85 ppb$_v$ limonene. (Error bars represent the SEM.)

We investigated the breath profiles of subjects exposed for 5 h to 85 ppb_v limonene, with measurements made prior to, during, and immediately after exposure. Considering the limonene abundance in exhaled versus inhaled air, an exhaled:inhaled concentration ratio of <1 indicates an uptake of this compound into the body (i.e. inhaled concentrations are higher in ambient air than in exhaled air), whereas a ratio of >1 demonstrates a release of limonene from the body (exhaled concentrations are higher than the surroundings). We found that limonene was readily taken up by the body during the exposure period and was subsequently released after exposure desisted (see fig. 2). This highlights how environmental exposure prior to conducting breath gas analysis can have a large impact on constituent exhaled compounds, which may be partly exogenous. Furthermore, exhalation of odorous compounds, such as those outlined above, can have an impact on olfactory sensitivity, which can be problematic for sensory science investigations.

Sensory science

Sensory science undertakes to establish the perception of various stimuli. In the case of olfactology, i.e. the study of the sense of smell, this typically involves offering an odorous stimulus to a test subject and monitoring physiological responses such as brain activity, breathing and/or heart rate, as well as other parameters. To augment such measurements, concentrations of odorants in the nose can be assessed to ascertain a correlation between physiological reactions and olfactory uptake. This has been hitherto practically impossible with standard off-line chemical analytical tools. However, PTR-MS has opened up this assessment possibility by providing the necessary time resolution and sensitivity for such analyses.

Olfactory perception of odorants

PTR-MS was used to monitor concentrations of applied odorants directly at the olfactory epithelium. Odorous stimuli – in the form of the compound diacetyl (2,3-butanedione), which has a butter-like aroma – were generated by an olfactometer and directed at the nostril, where test subjects were asked to sample the odour in different manners, either with a single sniff, rapid sniffs, or a forced inspiration. Intra-nasal odour concentrations were determined to be highest for a single sniff and lowest for a forced inhalation (see fig. 3).

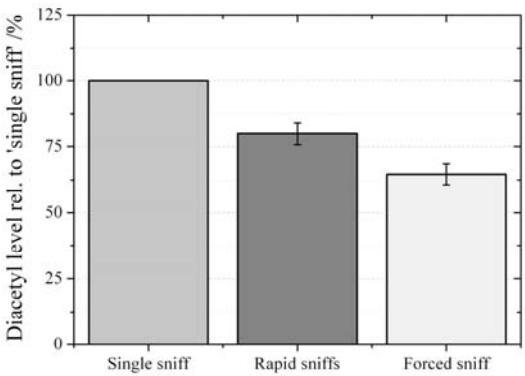

Figure 3: Intra-nasal concentrations of diacetyl at the olfactory epithelium.

This correlated with the perceived odour intensity reported by subjects and relates either to an increased dilution for the latter two sniffing modes, or is due to proportionally more gas bypassing the olfactory cleft. These findings are not only of importance from an olfactological viewpoint, but also for aroma perception in relation to food, as discussed in the literature [7].

Summary

The diverse research topics discussed in this paper demonstrate the widespread and yet common applications of PTR-MS for *in vivo* analyses, particularly of exhaled/inhaled breath. Such assessments benefit from the high temporal resolution, the low detection limits, precision and, importantly, from the insensitivity of the PTR-MS to gas humidity levels, which vary greatly between inhaled and exhaled gas. In summary, the PTR-MS technique is an excellent tool for application in the multidisciplinary environment of *in vivo* assessments, with possibly only the PTR-TOF system surpassing it in terms of versatility.

These studies also highlight the potential for false data interpretation due to insufficient sampling or exogenous compound backgrounds. In the former, metabolism of an ingested compound can proceed rapidly, providing only a brief opportunity to monitor its presence in exhaled breath. In the case of a slow metabolism, past administration of dietary supplements or previous environmental exposure prior to breath gas analysis can result in the exhalation of compounds that are not of endogenous origin. Thus, care must be taken when conducting breath gas analyses not to falsely attribute exhaled exogenous compounds to state of health or diseases.

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PTR-MS breath gas analysis during oral glucose tolerance test in gestational diabetes screening

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Abstract

The authors study the feasibility of human breath gas analysis via proton transfer reaction mass spectrometry (PTR-MS) as a diagnostic technique for gestational diabetes mellitus (GDM) screening. PTR-MS breath gas analysis allows a real-time, non invasive diagnostic procedure which can integrate many different screenings into a single test, saving time, cost and patient stress.

Standard medical practice includes a pregnancy screening where blood samples are taken during an oral glucose tolerance test (OGTT). This allows the measurement of various molecule concentrations in blood including glucose, which correlates very well to fetal as well as maternal complications.

The investigators collected two-hour long sequences of breath gas samples from 53 consecutive pregnant women undergoing GDM screening. The samples were analyzed on-the-fly by a proton transfer reaction mass spectrometry (PTR-MS) device connected to a buffered end-tidal (BET) sampler [Herbig 2008], allowing the measurements of the volatile organic compounds (VOCs) in the alveolar breath gas alone. Feature selection was performed by identifying a subset of PTR-MS mass signal sequences with an identifiable time evolution. Selected mass signal sequences were fitted either with a linear function $y = \mu x + c$ representing long-time evolution, or with an exponential function $y = axe^{-\beta x} + c$ representing short-time evolution. The following statistical analysis concentrated on the time evolution effects. Only a subset of the fitting parameters was therefore considered, namely the estimated speed parameters μ and β for each mass signal and patient. Such reduced data was organized into four groups by mean of the information provided by the screening diagnoses: GDM, IGT, healthy and borderline healthy donors. A multivariate analysis of variance (MANOVA) was performed as a feature extraction step, identifying linear classifiers and computing a properly defined separation score. A randomized permutation analysis was performed to obtain an indication of significance on the distribution of separating scores.

The authors obtained a coincidence of classification with standard diagnoses, the linear classifiers identifying the 4 subgroups without mismatches. The low permutation p-value of 12% suggests that this result is significant. Current work covers, among other topics, the identification of the most important mass signals involved by means of the weights of the linear classifiers and the bio-kinetic interpretation of the findings.

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PTR-MS detects rapid changes in volatile metabolite emission by Mycobacterium smegmatis after the addition of specific antimicrobial agents

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Abstract

The metabolic activity of plants, animals or microbes can be monitored by gas head space analysis. PTR-MS is rapid and can detect metabolic responses on line as they occur. Here, we study the headspace of actively growing cultures of paired ciprofloxacin sensitive and resistant bacterial strains (*Mycobacterium smegmatis* in Middlebrook M7H9 liquid media) after the addition of the antibiotics ciprofloxacin and gentamicin in real time. Following the emission patterns of the mycobacteria over time allowed volatile markers specific for the bacterial response to each antibiotic to be detected. A proportion of the measured responses were very rapid, occurring within three hours after the addition of the compounds and varied between isolates with different resistance phenotypes. We observed a two fold increase of m73 (unidentified C4 compound) within 10 hours after the addition of ciprofloxacin and a threefold increase of m45 (acetaldehyde) within 4 hours after the addition of gentamicin. Monitoring the emission of specific volatiles into the culture headspace thus has the potential for rapid drug susceptibility testing. Moreover, these and other differences in the measured responses to the two tested compounds provide evidence that monitoring multiple compounds may also give an indication of the mechanism of action of the compound added.

Breath Analysis with PTR-MS: More breath markers for lung cancer

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Abstract

In a clinical screening study we have measured several hundred subjects using real-time breath analysis with PTR-MS. We present and discuss potential breath markers for lung cancer with a critical view on the data analysis. The presented problems and solutions are also applicable to other analytical methods used in breath analysis.

Introduction

Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) is an analytical technique for detection and quantification of volatile organic compounds (VOCs) in air. The very sensitive PTR-MS instruments are capable of detecting VOCs in real-time and at extremely low concentrations (detection limit in the low pptv range). This makes PTR-MS instruments ideal tools for the non-invasive analysis of breath volatiles. Breath analysis with PTR-MS is a prosperous and constantly growing field of research [1]. Several challenges, arising in breath analysis (with PTR-MS), have been previously discussed: e.g. sampling process [2], optional sample storage [3], influence of the breath gas matrix, and quality assurance [4]. However, even with a "perfect" instrument the appropriate interpretation of the measured data still represents a major part of the challenge.

Judging from the numerous research projects with the same goal, the quest for lung cancer markers seems to be "the holy grail" of breath gas analysis. The severity of this disease and the lack of suitable screening methods make this an important target. Typically a set of several markers is reported, which in combination yield a good detection quality. As a result, the list of published markers is long with little to no overlap. This suggests that the signatures of lung cancer in breath are subtle and the interpretation of the data is difficult. Especially, when a multitude of markers is measured and the groups are not sufficiently large, the risk of finding coincidental correlations arises.

Methods

In a clinical screening study we have performed several hundred breath measurements using real-time breath analysis with PTR-MS [4]. We have used Buffered-End-Tidal (BET) sampling [2] to enhance the signal quality and to decrease testing time for the patient. In a typical analysis we have screened 160 m/z per person. The end-tidal value of each VOC was determined from five exhalations, to account for breath-to-breath variations.

We have focused on a careful and critical approach to the statistical analysis of the data. We have conducted extensive data mining to determine breath markers for lung cancer using five different algorithms. Only markers that are consistently confirmed by all algorithms are accepted as potential markers. The found markers are validated on an independent data set with a 10-fold cross-validation.

Most breath analysis instruments yield large numbers of measured variables, in our case 160 potential markers (m/z). In comparison, the groups of patients and controls are typically relatively small. We will show that in such a case the danger of finding coincidental correlations, so-called "Voodoo correlations", becomes apparent. To address this issue we have derived an intuitive "Voodoo test" in order to reveal the possibility of such correlations.

Results

To test the quality of the complete process from sampling over data analysis to results, we test the underlying set of data for known correlations. We find several breath markers that differ significantly between smokers and non-smokers, which are in good agreement to the literature [5], and would yield an almost perfect diagnostic breath test (AUC of 98.9%).

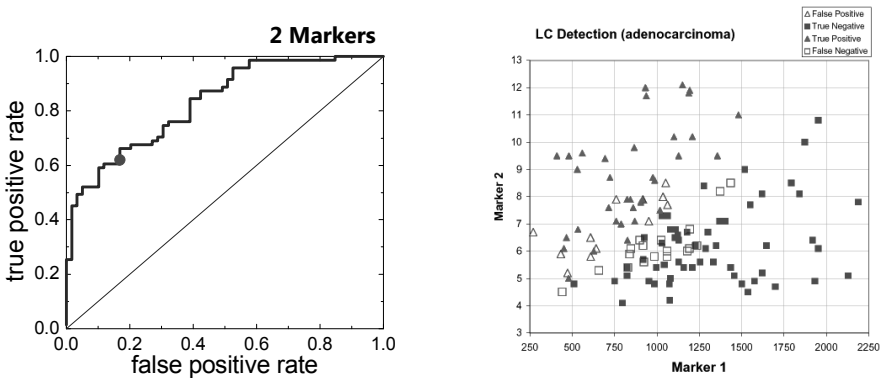

Figure 1: (left) ROC curve for a lung-cancer test with two markers. The area under the curve (AUC) is 83%. The dot on the curve marks the maximal Youden index, i.e. the optimal working point. (right) Data distribution for the two lung-cancer markers - in ncps. The closed symbols are true positive (triangles) and true negatives (squares). The open symbols are the respective false positive and false negatives.

In a next step we analyze the data for breath markers for bronchial adeno carcinoma. This histological type represents the largest group among the lung cancer patients and also yields the best results. The data set consists of breath measurements of 53 patients and 69 healthy controls

2 in figure 1 (right). In figure 1 (left) the resulting test is characterized by a receiver operating characteristic (ROC) curve. To quantify the quality of the underlying breath test for we calculate the area under the ROC curve (AUC) and obtain 83% with only the two markers (cross-validated), which would already constitute an excellent test. With two markers the results can be displayed in a two dimensional plot as depicted in figure 1 (right).

Finally, we analyze the markers by PTR-TOF. For m/z 99 we find two potential sum formulae: $C_6H_{10}O$ (e.g. Hexenal) or $C_5H_6O_2$ (e.g. Furanmethanol, 2-methyl-3(2H)-furanone). On m/z 69 is one compound: C_5H_8. Using PTR-TripleQuad-MS we can confirm that m/z 69 is consistent with Isoprene, as expected.

Discussion

In contrast to many studies, where long lists of lung cancer markers are presented, we have taken a more critical approach to data analysis. We identified “Voodoo correlations” as a potential problem, which is not limited to PTR-MS studies. By implementing methods with special attention to confounding variables and Voodoo correlations, we are able to identify two robust markers. One of these markers m/z 69, has also been observed in another study [6], confirming our results. The markers are specific for one type of lung cancer (bronchial adeno carcinoma) and yield an area under ROC curve of 83%. We have further analyzed the markers to get insight into their chemical composition using PTR-TOF. The presented problems and solutions are also applicable to other analytical methods used in breath analysis.

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The average composition of exhaled breath of healthy women by PTR-TOF-MS

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Abstract

We analysed the exhaled breath of a cohort of 50 healthy women using Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS). To ensure that end-tidal exhaled air was collected, we used a Breath Collecting Unit, which sampled breath gas only when the CO_2 signal was high. Samples were stored in inert Silco cans and analysed subsequently by PTR-TOF-MS. Components are characterized by their sum formula and were extracted from the raw data by matching them with a list of candidate compounds. A description of the average composition of the investigated cohort is given.

These data can be helpful to identify compounds in breath measurements with quadrupole PTR-MS systems, where a separation of isobaric compounds is not possible.

An innovative approach to the analysis of VOCs exhaled by mice under regular housing conditions at the German Mouse Clinic using hs-PTR-MS

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Abstract

The noninvasive method of breath gas analysis is widely used in human studies to explore the diagnostic potential of endogenous VOCs [1]. Proton transfer reaction mass spectrometry (PTR-MS) measures a wide spectrum of VOCs online, fast and nearly simultaneously from ppm (part-per-million) down to ppt (part-per-trillion) levels [2]. In the German Mouse Clinic (GMC) mutant mouse models for human diseases are comprehensively phenotyped to better understand the underlying molecular mechanisms and to develop new therapeutic strategies. Despite the advances in PTR-MS instrumentation the exploration of exhaled VOCs of small animals is still challenging and, hence, rather uncommon and furthermore restricted to specific VOCs as acetone or ethanol [3, 4]. Therefore, the aim of our study was to develop a PTR-MS setup suitable for unrestrained screening of exhaled VOCs in mouse models of human disease.

To develop a robust and efficient but also specific and highly automated phenotyping method for breath gas analysis of mice using hs-PTR-MS several challenges have to be addressed: scale the sampling of breath gas to the dimensions of a mouse, segregate VOC contaminations from urine, faeces, and food confounding the analysis from VOCs by mice and to detect distinct VOCs originating from exhaled breath of mice. The solutions to the above mentioned challenges led to a new, innovative approach composed of a 4-step strategy: (1) procedure to sort out profiles that are disturbed by environmental confounders, (2) identification of VOCs predominantly originating from exhaled breath, (3) determination of the source strength of a VOC and (4) adjusting the derived source strength of the VOCs to the different activity levels of mice which strongly affect the exhaled minute volume, and thus, the signal strength.

Based on the above described 4-step strategy we conducted a proof of principle study to demonstrate that metabolic changes due to a dietary intervention can be followed up by monitoring exhaled VOCs. The source strength of 24 breath-driven VOCs was determined in a

sample of 14 mice before and after feeding a purified high fat diet (60% of the energy from fat). Several breath-derived VOCs showed distinctly lower levels after feeding the high-fat diet compared to initial levels when fed the control chow, whereas one VOC was significantly elevated. These VOCs can be related to physiological functions and metabolic pathways and may be useful as markers for metabolic phenotyping.

In summary the novel approach to analyse exhaled VOCs of mice has a high potential in various screens of the GMC. The unrestrained, short-term stay of a mouse in the respiratory chamber is very compatible with the various screening methods in the GMC.

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Applications in Environmental Science

Measuring the dry depositional sink of oxidized organic vapors to vegetation using PTRMS

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Abstract

In recent years PTR-MS technology has played a significant role for quantitative analysis of Volatile Organic Compounds (VOC) in environmental sciences. Due to its rapid sample analysis capability PTRMS has been particularly useful in combination with micrometeorological measurement strategies. Analysis of oxygenated VOC (oVOCs) fluxes from past measurement campaigns reveals a significant uncertainty in the dry depositional flux of oVOCs

Introduction

Large quantities of volatile organic compounds (VOC) enter the atmosphere. The annual production of VOC (600 -2000 TgC/a) likely exceeds that of methane and CO (~500 TgC/a each). Together these gases fuel tropospheric chemistry. Oxidation of VOC leads to the formation of aerosol (Hallquist et al., 2009) via complex organic chemistry (e.g. Atkinson and Arey, 2003; Paulot et al., 2009) in the gas and aerosol phase thereby modulating the oxidation capacity of the atmosphere (Lelieveld et al., 2008). Currently one of the biggest uncertainties in constraining budgets of VOC is the amount of dry and wet deposition to vegetation, which acts as a major source and sink for organic trace gases on a global scale. This has consequences for constraining secondary species produced in the gasphase, which will either oxidize to CO and CO_2, condense on or form organic aerosol (OA) and be rained out, or directly deposit to the surface via dry and wet deposition. Two recent bottom-up assessments of the tropospheric OA budget (Hallquist et al., 2009, Goldstein and Galbally, 2007) were based on varying assumptions for wet and dry deposition of organic vapors (i.e. 200±100 TgC/a vs 800 TgC/a) and consequently derived significantly different global production rates for secondary organic aerosol (SOA).

Results and Discussion

We present a synthesis of ecosystem scale flux measurements using PTRMS technology conducted over the last 7 years showing that the removal of oxygenated VOC (oVOC) via dry deposition is significantly larger than currently assumed for deciduous ecosystems. A revised oVOC uptake scheme, incorporated into a global chemistry-transport model, predicts appreciable regional changes in annual dry deposition fluxes. We estimate a lower and upper bound for the annual deposition flux of gas phase oVOCs between 37-56% relative to the annual VOC emission flux on a carbon basis.

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Boreal Forest VOC Measurements using a Cold Trap PTR-MS System

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Abstract

Proton Transfer Reaction Mass Spectrometry (PTR-MS) measurements of volatile organic compounds (VOCs) from a boreal forest field station in Hyytiälä, Finland (Latitude 61° 51' N; Longitude 24° 17' E) will be presented. Measurements were acquired from above the coniferous forest canopy between July and August 2010 as a part of the HUMPPA Campaign. A cold trap inlet system, based on the work of Jobson and McCosky 2010, was developed at the Max Planck Institute and field tested upstream of the PTR-MS to reduce the water concentration of the sample. In laboratory studies this was found to improve sensitivity when operating the PTR-MS at lower drift tube voltages by reducing potential interference from water cluster ion formation and the back reaction of ions with water. The field dataset generated using the quadrupole PTR-MS and cold trap will be used to show the various local and regional influences affecting the site. These include the biogenic emissions from the surrounding forest, occasional biomass burning plumes, and other anthropogenic sources. The source of the burning events was identified as the Novgorod region of the Russian Federation, some 400 km east of Moscow. Biomass burning signatures were observed in the masses attributed to hydrogen cyanide (m/z 28), formaldehyde (m/z 31), acetonitrile (m/z 42), methanol (m/z 33) and acetone (m/z 59).

Ultrafast "fingerprinting" of volatiles emitted after leaf wounding and darkening performed by Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF)

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Introduction

A multitude of biogenic volatile organic compounds (BVOCs) can be emitted in response to abiotic [1] and biotic [2] stress conditions. In particular, mechanical damage of leaf tissues represents a critical abiotic stress to which plants are exposed in nature during their whole life cycle.

The green leaf volatiles (GLVs) are a blend of aldehydes and alcohols mostly belonging to the hexenyl (C6) family ubiquitously generated and promptly released by all plant species [3] after membranes breakdown in response to adverse environmental conditions such as drying [4], freezing [6], or herbivory outbreaks [6]. The same mixture of GLVs is emitted in healthy leaves, together with a spike of acetaldehyde [7], during fast transition from light to dark conditions.

Proton transfer reaction mass spectrometry (PTR-MS) was successfully employed to monitor real-time emissions of leaf volatiles as a consequence of wounding, drying, freezing events and after leaf darkening. However, only few masses could be tracked, in order to achieve fast and highly sensitive responses. This is a limit to the investigation when complex suites of compounds are rapidly emitted.

We used the recently developed proton transfer reaction - time of flight (PTR-TOF) mass spectrometry [8, 9] to improve the detection of BVOCs induced by wounding and darkening.

PTR-TOF records full mass spectra with a time resolution of less than one second and with a limit of detection of a few pptv. These features combined with a high mass resolving power ($m/\Delta m \sim 4000$) allow to distinguish different ions by providing exact mass weight and sum formula information thus making unambiguous identification of isobaric compounds possible. In addition, the time-of-flight detector has a higher efficiency to transfer higher molecular weight ions than the quadrupole system and therefore shows strongly reduced detection limit for compounds with high mass to charge (m/z) ratios.

We tested whether, by enhancing real-time detection through the use of PTR-TOF, the complex blend of BVOCs rapidly released upon leaf wounding or darkening could be further inspected. In particular, we focused on the kinetic of appearance of GLVs and on the suites of compounds released after wounding in turn reflecting their biosynthesis by activation of specific enzymes or their presence in storing structures within the leaves tissue.

Experimental Methods

The proton transfer reaction "time of flight" mass spectrometer (PTR-TOF) developed by the University of Innsbruck [8, 9] and commercially available by Ionicon Analytik GmbH (Innsbruck, Austria) was used. The basic PTR-TOF instrumental set up resembles the PTR-MS one [10], but PTR front part consisting of a hollow cathode ion source and the drift tube has been interfaced with a high mass resolution, orthogonal acceleration, reflectron time-of-flight mass spectrometer TOF-MS (Tofwerk AG, Switzerland). The resulting highly resolved mass spectra ranging between m/z = 20 and m/z = 315 were recorded every second. The raw PTR-TOF data are acquired by the TofDaq software (Tofwerk AG, Switzerland) and post processed by routines functions programmed in Matlab R2009b, 7.5 (The MathWorks Inc., Natick, MA, USA) [11].

We applied PTR-TOF to enclosure systems in order to real time monitor the complete release of BVOCs by leaves of plants constitutively emitting isoprene (Populus alba), monoterpenes (Quercus ilex), no isoprenoids (Dactlylis glomerata, Trifolium pretense, Ranunculus acris) or storing monoterpenes (Citrus limon) after wounding and darkening in controlled environmental conditions.

Results

Wounding: leaf wounding produces membranes breakdown and consequent oxidation of unsaturated fatty acids catalyzed by the activity of LOX and HPL enzymes, which results in a fast and transient evolution of a mixture of GLVs consistently with previous reports [12, 13]. However, the highly resolved kinetic of appearance of single compounds recorded by PTR-TOF now unambiguously reflects the different stages of the lipoxygenase biosynthetic pathway, and may even be used to derive in vivo the time course of enzyme activation and of substrate transformation.

The standardized conditions of our experiments allowed to validate whether the emission of wound-induced BVOCs is proportional to the extent of the foliar injury. Indeed, a linear correlation between the extent of wound produced and the emission of the most representative GLVs m/z 81.070 (hexenals) and m/z 83.086 (hexenols and hexanal) was found. Thus, GLVs represent an accurate proxy of the mechanical injury and a realistic indication of membrane deterioration [14].

PTR-TOF further complemented the analysis of BVOCs released after wounding *D.* glomerata leaves by detecting the fast release of pentanol (as fragment - $C_5H_{11}^+$ at *m/z* = 71.086) and pentenone (*m/z* = 85.064), acetaldehyde (*m/z* = 45.034), a burst of methanol (*m/z* = 33.034) and a protonated C_5H_8 compound with *m/z* = 69.070 that could be assigned to isoprene. Moreover, when cutting separately different forbs and graminoids plants of a mountain grassland ecosystem, PTR-TOF real time full mass spectra allowed to discover a species-specific isoprenoids storing capacity since a release of sesquiterpenes (*m/z* = 205.064) was shown only in *Trifolium repens* and an emission of monoterpene (*m/z* = 137.133) was found only in *Dactlylis glomerata* leaves.
A few minutes of dark adaptation, as well as exposure to different light intensities before wounding did not affect either the amount or the relative abundance of the GLVs emitted. However, a general impairment of the overall lipoxygenase pathway producing GLVs was observed *in vivo* and at whole plant level in *D. glomerata* leaves maintained in dark conditions for 7 days long.

Light-Dark transitions:
PTR-TOF was here exploited to analyze the rapid release of GLVs, together with a burst of acetaldehyde, in intact leaves during rapid fluctuations from light to dark conditions [7]. The ultrafast and complete PTR-TOF detection allowed to identify a species-specific blend of BVOCs triggered by a sudden change form light to dark condition in plants characterized by constitutive isoprenoids emission (*Populus alba*, *Quercus ilex*), no emission (*Dactlylis glomerata*) or isoprenoids storing capacity (*Citrus x limon*).
In particular, we found a very good relationship between the constitutive level of emitted isoprenoids (isoprene by poplar or monoterpenes by oak) and the maximum value of acetaldehyde detected during the burst occurring in light to dark transitions.

Discussion

PTR-TOF was successfully used to investigate BVOCs emission from plants in enclosure systems by recording full mass spectra with a high time and mass resolution and with a limit of detection of a few pptv. It allowed identification of species-specific suites of compounds by measuring “volatile fingerprints” rapidly emitted from leaf wounding and after transitions from light to dark conditions revealing new aspects of plant biodiversity with intriguing ecological connections (Brilli et al. submitted).
PTR-TOF seems to be particularly suitable to instantaneously link rapid enzymatic reactions or other biochemical *in vivo* processes with the detection of volatile products. The PTR-TOF high time resolution of BVOCs detection, which is lacking from many conventional analytic methods, makes PTR-TOF especially applicable as a novel technique to accurately dissect time course of stress-induced responses and use volatiles as markers for the enzymatic steps involved in these responses.

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What can we learn from year-round BVOC disjunct eddy-covariance measurements? A case example from temperate forest.

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Abstract

Long term ecosystem-scale biogenic volatile organic compounds (BVOC) flux measurements by disjunct eddy-covariance are needed to determine and characterize the BVOC emissions/depositions from episodic events (budburst, stress) as well as the continuous emission/deposition during vegetation growth and its seasonal evolution in interaction with climate and environment. If the data coverage is sufficient, this technique has the potential to provide a dataset covering the whole spectrum of meteorological and phenological conditions encountered by the studied ecosystem ending in a statistically more robust dataset than what can be provided by other BVOC measurement techniques. In addition, long term measurements allow in Oxygenated VOCs (OVOCs) depositions to be estimated in a realistic manner with is not the case with the enclosure technique.

Here we present a year-round campaign of disjunct eddy-covariance BVOC fluxes above a mixed temperate forest performed in the frame of the IMPECVOC (Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems) project. We will analyse the three main BVOC species (isoprene/monoterpenes and methanol) in order to illustrate the interest of long-term flux measurements by investigating the main driving variables and the underlying mechanisms of emission/deposition, how *de novo* carbon allocation to the isoprene/monoterpenes skeleton structure is altered through the time. For methanol, we will show the importance of deposition on a long-term basis and use an empirical model to discriminate the physical and physiological components of the exchange.

Introduction

Global BVOCs emission rates by terrestrial vegetation are estimated to be 700-1000 TgC y^{-1} [1] corresponding to nearly 90% of global VOC emissions. These emissions represent a major source of reactive carbon to the atmosphere that can influence the level of tropospheric ozone, the lifetime of other chemical compounds such as methane and the production of secondary organic aerosols, which can have both direct and indirect influence on the Earth's radiative budget [2].

Large uncertainties on global BVOC emission estimations result from the incomplete understanding of emission/deposition mechanisms depending on climate, environment and

vegetation physiology. BVOC emission measurements at different level scales (leaf, branch, ecosystem) are mostly limited in time, are operated during good climatic conditions and rarely cover the seasonal evolution. The best technique for long-term monitoring BVOC emissions in real conditions and at the ecosystem scale without disturbing the ecosystem is the disjunct eddy-covariance used in this study. In addition, the BVOC fluxes are measured simultaneously with carbon dioxide fluxes, which provide valuable information to better understand the BVOC production mechanisms. Our dataset extends from July to October 2009 and from April to October 2010 thus covering the Belgian spring, the summer and the first part of autumn. With this large data set, we have tried to extract the mechanisms of BVOC emission/deposition in relation with the seasonal evolution of vegetation.

Experimental Methods

Measurement site

The forested site is at Vielsalm in the Belgian Ardenne forest (50°18'18.20''N, 5°59'53.15''E altitude: 450 m). The climate is temperate maritime. The vegetation is a mixture of coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco), Norway spruce (*Picea Abies* [L.] Karst.), Silver fir (*Abies alba* Miller), and deciduous species, mainly beeches (*Fagus sylvatica* L.).

Methodology

The technique used to measure ecosystem BVOC fluxes was the disjunct eddy-covariance (DEC) [3]. The flux was computed as the covariance of vertical wind velocity component (measured by a sonic anemometer at a sampling frequency of 20.8 Hz) and BVOC concentration measured by PTR-MS. The ion signal intensities of the masses of interest were measured in a cyclical way, ending in a disjunct concentration time series for each mass. We measured the ion signals at mass-to-charge (*m/z*) ratios 21, 33, 39, 45, 59, 69, 71, 81, 87 and 137. The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. The PTR-MS was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2). During the measurements, the instrumental background was determined every 4 hours. The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every two or three days using a gravimetrically prepared mixture of these gases in N_2.

The sonic anemometer was placed at the top of a tower at a height of 52 m. Ambient air was continuously sampled close to the sonic anemometer through a main sampling line (PFA tubing) 60 m long and 6.4 mm inner diameter and was slightly heated above ambient temperature. A part of this air flow was drawn into the PTR-MS through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The time lag of the tube sampling was about 14.8 s. Measurements of turbulent CO_2 flux and relevant meteorological variables were also performed every half an hour.

Results and discussion

Up to now, we have investigated the isoprene/monoterpenes fluxes between July and September 2009. We have also studied the methanol fluxes and developed a model to better understand the physical and physiological mechanisms controlling the emission/deposition.

Isoprene/monoterpenes

During the day, isoprene and monoterperne fluxes were mainly controlled by the air temperature and the light. The seasonal evolution of the isoprene/monoterpene emissions was studied using a monthly temperature (C_T) and light (C_L) dependence function deduced from our results to standardize the fluxes. A seasonal decrease in the standard emission factors was observed (figure 1), probably linked to acclimation or senescence. The standard emission factor (30°C, 1000 µmol m^{-2} s^{-1}) fell from 0.91 ± 0.01 to 0.56 ± 0.02 µg m^{-2} s^{-1} and from 0.74 ± 0.03 to 0.27 ± 0.03 µg m^{-2} s^{-1} for isoprene and monoterpene fluxes respectively.

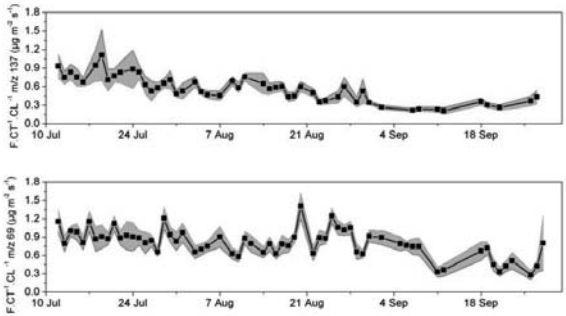

Figure 1: Mean diurnal evolution (PPFD > 300 µmol m−2 s−1) of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PPFD (1000 µmol m−2 s−1). The grey area represents the 95% confidence intervals.

During the night, a slight positive flux of monoterpenes was observed that seemed to be driven by air temperature. These night emissions were probably due to the volatility of monoterpenes stored in the needle resin ducts of coniferous species. There could also be a contribution from the soil through litter decomposition, from roots or from micro-organisms. The standard emission factor (30°C) for night-time monoterpene fluxes was equal to 0.093 ± 0.019 µg $m^{-2}s^{-1}$.

Finally, we studied the seasonal evolution of the relationship between the gross primary production and the isoprene/monoterpene fluxes. A linear relationship was observed, highlighting the strong link between carbon assimilation and isoprene/monoterpene emissions (figure 2).

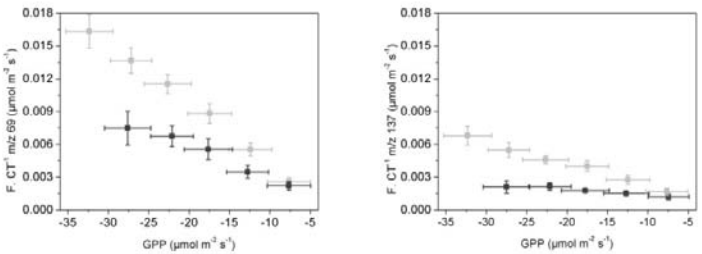

Figure 2: Bin averages of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C (n≥14, error bars are 95% confidence intervals) in relation to the gross primary production (GPP) for July (light grey) and September (dark grey).

Methanol

The methanol fluxes were bi-directional, generally negative (deposition) during the night and generally positive during the day. During the summer-autumn period, the night depositions were more important than the day emissions, the inverse situation was observed during the spring period. The methanol deposition increased linearly with friction velocity and with atmospheric methanol concentration. The humidity seemed to be also an important driving variable, the depositions being more important when the atmospheric water vapor pressure was closed to saturation. In these humid conditions, water films are initiated and favored on the vegetation surface. The methanol being very soluble in water, the deposition of methanol is enhanced by the presence of these water films.

In order to quantify the non-biogenic methanol exchanges, we developed a model of absorption/desorption, based on the two-layer model of Liss and Slater (1974) [4]. It took atmospheric methanol concentration, friction velocity, water vapor pressure deficit and Henry's law constant depending on temperature into account. The model was calibrated on night deposition fluxes measured during the summer-autumn of 2009 and validated on 2010 data. Simulation reproduced well measurements during most of the measurement period, as well in summer-autumn 2009, as during summer 2010. This suggests that, most of this time, the measured fluxes (night and day) can mainly be explained largely by a physical absorption/desorption process. In contrast, during one 2010 spring week, significant differences appeared between simulation and measurements (figure 3), suggesting the pre-eminence of biogenic fluxes. They appeared during a period presenting a co-occurrence of sunny conditions and important leaf development. These biogenic emissions corresponded probably to the demethylation of pectin in the primary cell walls and were mainly controlled by the air temperature.

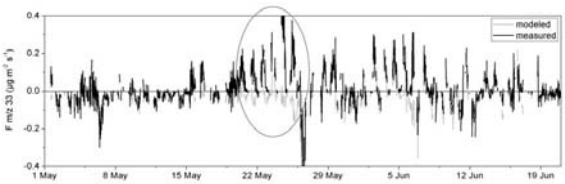

Figure 3: Representation of measured and modelled fluxes of methanol (m/z 33) during May-June 2010 period.

Acknowledgements

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OH Reactivity Measurements using PTR-MS: Branch Enclosure Applications

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Abstract

We developed an OH reactivity measurement system to measure total OH reactivity from branch enclosure using a comparative reactivity method (Sinha et al., 2008). This system has the advantage of measuring a wide dynamic range of total OH reactivity (few tens to few hundreds s^{-1}) along with BVOC emissions. This allows comparisons of temporal variations of measured and calculated total OH reactivity. We deployed the system at the PROPHET tower measurement site in Pellston, Michigan U.S. as a part of the CABINEX 09 (Community Atmosphere Biosphere Interactions Experiments) field campaign.

Introduction

Unexplored BVOC and their oxidation products have been speculated as a main source of uncertainty for understanding tropospheric photochemistry, controlling ozone and secondary organic aerosol formation on regional and global scales. For this reason, many studies have assessed abundances of unexplored BVOC. One of the most effective ways to quantify unexplored BVOC is comparison between measured and calculated OH reactivity. Previous results in ambient air of various forest canopy environments have consistently indicated that a significant fraction of measured OH reactivity could not be explained by measured BVOC and their oxidation products. This unaccounted OH reactivity has been termed "missing OH reactivity" and there is still controversy about the origins of missing OH reactivity (i.e. whether it is coming from unexplored BVOC emissions or unexplored oxidation products from known BVOC). To constrain potential sources of unexplored BVOCs, we conducted branch enclosure OH reactivity measurements for four different dominant tree species at the PROPHET site (Pellston, MI USA) during the CABINEX field campaign in 2009.

Experimental Methods

Figure 1 shows a schematic diagram of the branch enclosure-PTR-MS system used to measure total OH reactivity along with BVOC emissions. 3-5 slpm of zero air was pumped into a ~ 2 liter Teflon enclosure maintaining a residence time less than 1 minute. Air from the enclosure was introduced into a glass reactor, where total OH reactivity was measured according to Sinha et al. (2008). During OH-reactivity measurements, we occasionally filled cartridge samples to obtain speciated BVOC information using GC-MS analysis.

Figure 2 shows a multi-point calibration curve using known VOC mixtures. It shows excellent linearity over a wide OH reactivity range. The limit of detection calculated from this analysis is ~ 15 s^{-1}.

Results

Figure 3 presents temporal variations of measured OH reactivity and calculated OH reactivity from measured isoprene concentrations by PTR-MS. The results were obtained from an oak branch, the main isoprene emitter in this ecosystem. Two traces in the figure show reasonable agreement indicating no strong emissions of unidentified BVOC. We conducted the measurement for three other major tree species in the ecosystem; in most cases the measured OH reactivity can be reasonably explained by the temporal variations of calculated OH reactivity, assessed from the measured concentrations of the major BVOC (isoprene and monoterpenes). The results indicate that we probably have a good understanding of BVOC emissions from this ecosystem. Further discussion on possible sources of ambient missing OH reactivity and analytical characteristics will be presented.

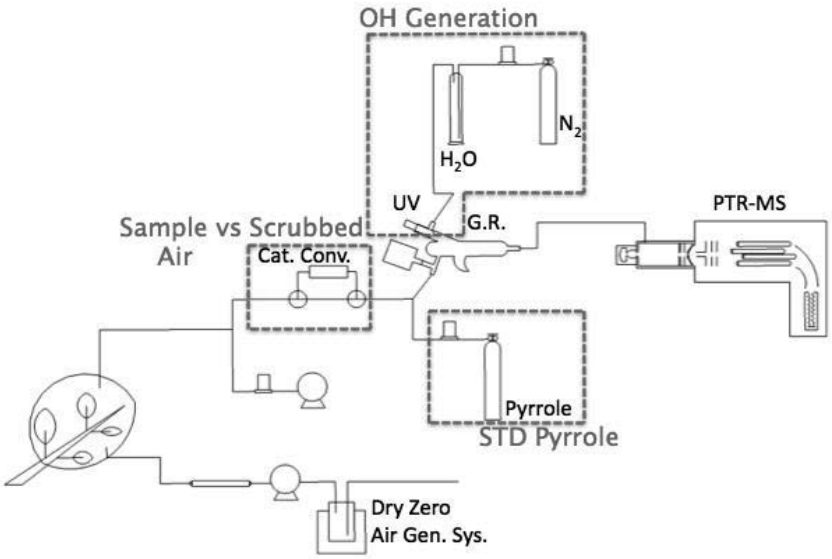

Figure 1: A schematic diagram of an OH reactivity system for branch enclosure measurements

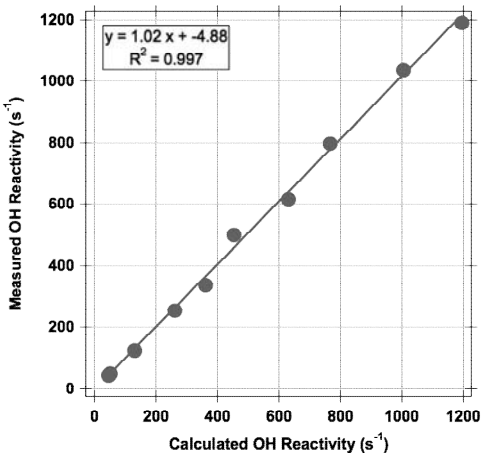

Figure 2: Multi-point calibration results

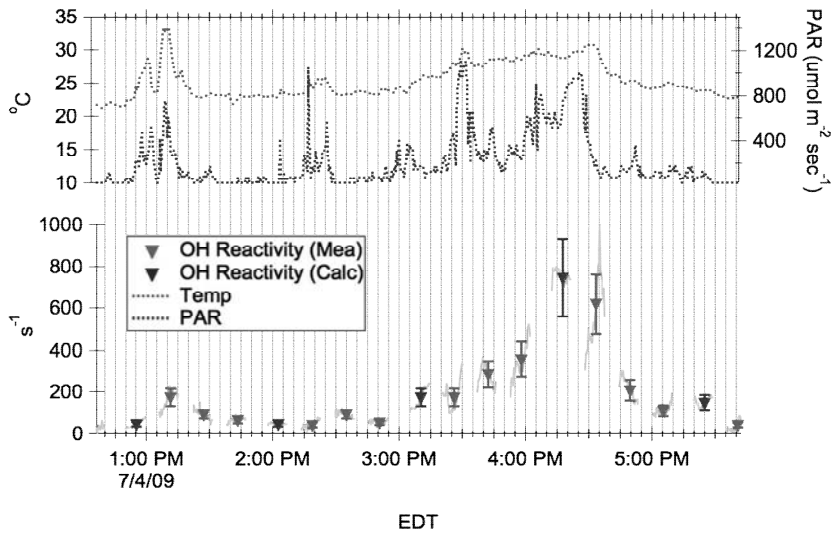

Figure 3: Temporal variations of measured OH reactivity, calculated OH reactivity, temperature and PAR of an Oak tree enclosure.

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Alumina Refining and Air Quality: Using PTR-MS to measure VOCs and Odour from the Bayer Process

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Abstract

Emission of volatile organic compounds (VOCs) and generation of odour may be an unwanted consequence of the Bayer Process which is used to refine alumina from bauxite ore. This arises primarily when bauxite and associated organic material is combined with concentrated hot sodium hydroxide at elevated pressures, leading to decomposition and subsequent volatilization of organic matter to the atmosphere. In Australia, emissions and odour from alumina refining have been of significant concern to communities located near some refineries. The basic science of VOC and odour generation in the Bayer Process is largely unknown and there is little information in the scientific literature about VOC emissions from the Bayer Process. Here we use PTR-MS to characterize and understand the chemical processes influencing the generation of VOCs and odour in the Bayer Process and processes related to alumina refinery Digestors, Calciners, Liquor Burners, Red Mud, and Waste Water. Understanding these processes will allow control strategies for VOCs and odour to be designed, resulting in improved air quality surrounding refineries.

The PTR-MS has been used in three separate studies. The objective of the first study was to determine the identity and sources of VOCs in air in ambient air south of the Alcoa World Aluminum refinery at Wagerup, Western Australia. In 2006 a field campaign was undertaken over 60 days in which VOC and other air pollutant measurements were made at a site approximately 2 km south of the main refinery emission stack [1]. The measurement site was approximately half way between the Refinery and Yarloop, a small town with a history of odour and other complaints relating to the Refinery emissions. Supplementary measurements of VOCs using DNPH cartridges and adsorbent tube assisted with PTR-MS mass identification.

The objective of the second study was to measure the range of organic compounds present in point source samples from the refinery and examine their possible connection to refinery odour. The source samples were collected from 6 distinct refinery point sources and analysed for VOCs using PTR-MS. Source samples were analysed for odour by the standard dynamic olfactometry method at The Odour Unit, Perth WA.

The objective of the third study was to undertake laboratory studies to characterize VOC and odour emissions from slurry mixtures simulating bauxite milling and desilication sub-processes. Bauxite was reacted with Bayer liquor at atmospheric pressure and at temperatures up to 90ºC and the headspace gas was sampled directly by PTR-MS and also collected on to adsorbent tubes for GC-MS-FID/Olfactory analysis.

In the first study, single candidate compounds were identified for 11 of the 24 masses detected at measurable concentrations in ambient air. Analysis by wind direction showed that protonated

mass 59 (acetone), 45 (acetaldehyde), 33 (methanol) 43 (multiple compounds) and NO_x have sources in the direction of the Refinery consistent with the Wagerup Refinery Emissions Inventory. On two occasions odours were observed when wind blew from the direction of the refinery which coincided with an increase in acetone and NO_X. However the measured acetone concentrations were below the odour detection threshold and the compound(s) responsible for the odour could not be determined.

In the second study, indicative total VOCs (TVOCs) in the point source bags ranged from 5 - 215 ppm. Masses 33 (methanol), 43 (multiple compounds), 45 (acetaldehyde) and 59 (acetone) occurred at the highest concentration in the samples. There was a non-linear relationship between total odour concentration and TVOC concentration in the samples.

In the third study, the VOCs present in the highest concentrations in the headspace of the bauxite and liquor at 90ºC were mass 59 (acetone), 33 (methanol), 45 (acetaldehyde) and 73 (methyl ethyl ketone). GC-MS-FID/Olfactory analysis of adsorbent tube samples collected is underway.

This work demonstrates the applicability of PTR-MS techniques to better understand the complex processes resulting in VOC emissions during alumina refining. This work suggests there are a number of key emitted VOCs which are common to several stages of the alumina refining process. Further laboratory experiments are planned including measurements of headspace gas from the digestion of bauxite under digestion temperatures and pressures of 150°C-280°C, and up to 7500kPa, as well as effluent from calcining and liquor burning processes.

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Emission and deposition of VOC from/to a mountain grassland: an eddy covariance case study using a PTR-TOF

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Abstract

Eddy covariance (EC) requires fast response measurements (5-20Hz) for best performance and is the preferred technique for high time resolution measurements since it is the only direct flux determination method. Proton transfer reaction ionizes a wide range of volatile organic compounds (VOC); and in combination with a time of flight mass spectrometer (PTR-TOF) it was used to measure at 10 Hz frequency full mass spectra up to m/z 315. The mass resolution of the PTR-TOF (1,2) enabled the identification of chemical formulas and separation of oxygenated and hydrocarbon species exhibiting the same nominal mass. >From the full mass spectra, we determined 481 ion mass peaks (3) from ambient air concentration above a managed, temperate mountain grassland in Neustift, Stubai Valley, Austria. Eddy covariance fluxes were calculated for all of the ion mass peaks for time periods of fully grown grass, harvesting (cutting and drying) as well as during the start of re-growth after harvesting (4). During harvesting we found significant fluxes of 18 compounds distributed over 43 ions, including protonated parent compounds, as well as their isotopes and fragments and VOC-H^+-water clusters.

The dominant BVOC fluxes were methanol, acetaldehyde, ethanol, hexenal and other C_6 leaf wound compounds, acetone, acetic acid, monoterpenes and sequiterpenes. The smallest reliable fluxes we determined were less than 0.1 nmolm^{-2} s^{-1}, as in the case of sesquiterpene emissions from freshly cut grass. During cutting, total VOC emission fluxes up to 200 nmolCm^{-2} s^{-1} were measured. Methanol emissions accounted for half of the emissions of oxygenated VOCs and a third of the carbon of all measured VOC emissions during harvesting.

The measurements of VOC fluxes above the harvested grassland are used as a case study of EC flux determination of reactive species. The use of EC for CO_2 and heat flux calculations has become a well benchmarked and analyzed routine. However, measurements of reactive species

with the continuous high time resolution required for the use of EC has only recently become possible due to development of instruments enabling 2-20 Hz measurements of VOCs, ozone and aerosols. However, the calculation routines for inert gases cannot be directly applied to VOCs since reactivity is an extra challenge to the flux interpretation and the flux protocols must take into account the used measurement technique. We will discuss the VOC fluxes during grass harvesting as a case study for the technical requirements of the EC measurements and data post processing in the case of PTR-TOF measurements.

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Application of the PTR-MS for Indoor Related Test Chamber Studies

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Introduction

The indoor environment is a multidisciplinary scientific field involving chemistry, physics, biology, health sciences, architecture, building sciences and civil engineering. The need for reliable assessment of human exposure to indoor pollutants is attracting increasing attention. This, however, requires a detailed understanding of the relevant compounds, their sources, physical and chemical properties, dynamics, reactions, their distribution among the gas phase, airborne particles and settled dust as well as the availability of modern measurement techniques [1].

Real-time monitoring is an effective way to measure time fluctuating concentration levels which are frequently found indoors. If a temporally high resolution concentration profile or peak values are to be determined, continuously recording instruments would be indispensable. Proton-Transfer-Reaction-Mass-Spectrometry (PTR-MS) allows the monitoring of selected $[M+1]^+$ ions, the high time resolution makes it a powerful tool for indoor related research [2]. This was recently demonstrated by Weschler and colleagues, who have used PTR-MS for investigating squalene-ozone surface chemistry [3].

We successfully apply the PTR-MS technique for time-resolved measurement of selected compounds in our environmental test chambers if highly dynamic processes are considered. Two types of experiments will be outlined in more detail: a) the monitoring of VOCs during operation of electronic office equipment [4,5] and b) the determination of diffusion coefficients in building materials [6].

Experimental Methods

The diffusion of VOCs through building materials can be experimentally determined in a glass double-climate chamber with an interior volume of 24 L each (Fig. 1A). For the present study the climatic conditions were 23°C and 50% r.h. on both sides while the air exchange rate was set to 2.5 h^{-1} in the chamber that contains VOCs (chamber 1) and 0.5 h^{-1} in the target chamber (chamber 2). A high-sensitivity PTR-MS (IONICON) was attached to both chambers by solenoid valves at a switching interval of 5 min. Toluene was led into chamber 1 from a constant diffusion source. A gypsum fiber board (thickness 1 cm) was placed between chamber 1 and 2. The migration of the toluene through the material (0.0314 m²) was monitored at m/z 93 in chamber 2.

The release of ultrafine particles and VOCs from a b/w laser printer was studied in a 1 m³ glass chamber (see Fig 1B). Two consecutive measurements (5 min printing time each) were performed at 23°C and an air exchange rate of 1.5 h^{-1}. The relative air humidity was set to ~5% at starting conditions. The area coverage of the printed template was 0% and 20%, respectively. The measurement of particle concentration and size distribution was performed using a fast mobility particle sizer (FMPS, TSI Inc.) which measures the particle number concentration in the range of 5.6 - 560 nm in 32 channels every second. Styrene (m/z 105) and benzaldehyde (m/z 107) were mea-

sured by use of a high sensitivity PTR-MS (IONICON). Ozone was added into the chamber to investigate the chemical reactivity of emitted particles and VOCs.

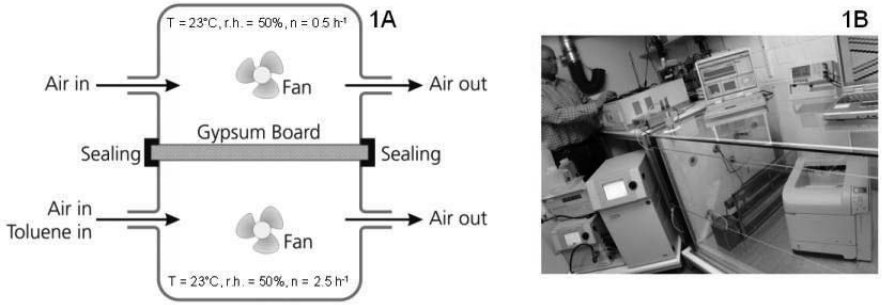

Figure 1: Experimental setup for measuring diffusion of VOCs in building products in the glass double-climate chamber (1A) and experimental setup for measuring particle and VOC emissions from office equipment in the 1 m³ glass chamber (1B).

Results and Discussion

Diffusion Experiment

The results of the diffusion experiment are shown in Fig. 2. In chamber 1 the toluene steady-state concentration was reached within 2 h as predicted by the air exchange rate of 2.5 h^{-1}. Due to the diffusion process reaching of the steady-steady state was delayed in chamber 2. Both curves could be fitted with a single exponential function $C(t) = C_{\infty} \cdot [1-\exp(-n \cdot t)]$.

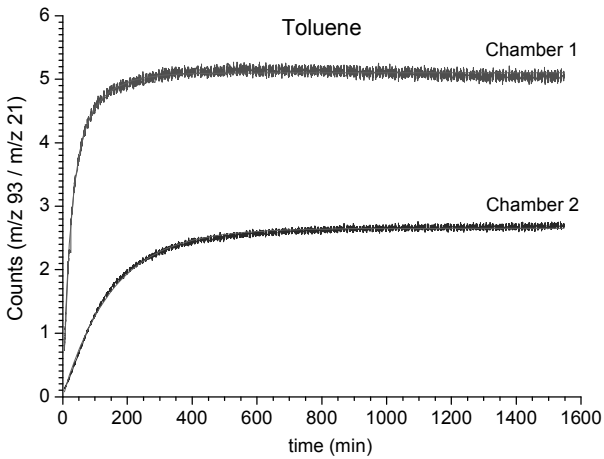

Figure 2: Results of the double-climate chamber experiment. Toluene was led into chamber 1 and diffused into chamber 2 through the gypsum board.

The diffusion coefficient $D_{Tol} = 0.0037$ m² h^{-1} was then calculated from Equation (1) with $\dot{V} = 0.012$ m³ h^{-1}, dx = 0.01 m, A = 0.0314 m².

$$D = -\frac{V \cdot dx}{A} \cdot \frac{C_{\infty}^{Chamber\,2}}{C_{\infty}^{Chamber\,2} - C_{\infty}^{Chamber\,1}} \quad (1)$$

This value is in excellent agreement with previous results reported by Meininghaus and Uhde [6], who determined coefficients between 0.0025 $m^2\ h^{-1}$ and 0.0030 $m^2\ h^{-1}$ for the diffusion of toluene in gypsum boards. It is a big advantage of the method that in the time-independent case (see Equation 1) absolute concentrations are not required. The diffusion coefficient can be directly obtained from the ratio of ion counts measured in chamber 1 and chamber 2.

Laser Printer Experiment

Laser printers are a potential source of ultrafine particles, volatile (styrene, toluene, xylenes, etc.) and semi volatile (siloxanes, aliphatic hydrocarbons, etc.) organic compounds, in indoor environment, especially in office rooms. The results of many studies have shown that the particles do not originate from primary sources like toner dust but are formed as secondary organic aerosols (SOA) from nucleation and condensation processes. Destaillats et al. [7] have hypothesized a possible role of ozone chemistry in the formation of ultrafine aerosol, since ozone is also produced during printing. It is therefore of interest to investigate the influence of ozone on emitted particles and organic compounds. As far as VOCs are concerned, styrene and its byproduct benzaldehyde are interesting target compounds, because styrene is commonly emitted from laser printers and known to be ozone-reactive. This, however, brings up analytical problems, because Tenax TA, a convenient VOC adsorbent, decomposes in a reactive atmosphere [8]. Moreover, the time resolution of Tenax TA sampling followed by GC/MS analysis is not sufficient for the monitoring of fast dynamic processes. In this case PTR-MS is the method of choice because this technique allows a highly selective online measurement of both substances in the chamber air at m/z 105 and m/z 107, respectively.

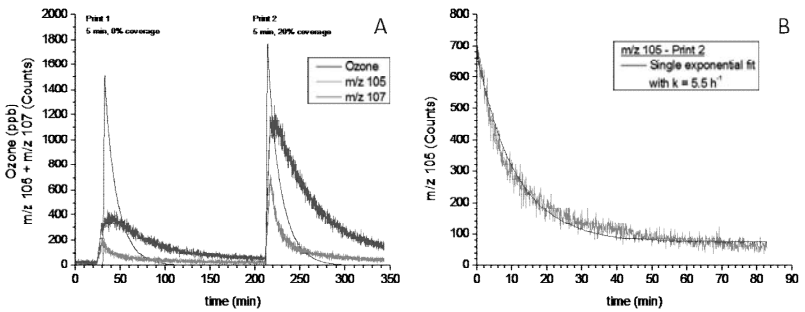

Figure 3: Time vs. concentration profiles of ozone, m/z 105 (styrene) and m/z 107(benzaldehyde) before, during and after printing (3A). Single exponential fit $C(t) = C_0 \cdot exp(-k \cdot t) + y_0$ to the m/z 105 decay curve of print 2 (3B).

The data shown in Fig. 3 were extracted from an ongoing study. The increase of the m/z 105 and m/z 107 PTR-MS signals after start of the printing process is clearly visible (see Fig. 3A). The addition of ozone (measured online by UV-spectroscopy at 248 nm) had no effect on the distribution and concentration of ultrafine particles (figure not shown). At this stage we are not able to identify the source of benzaldehyde, which could be emitted from the printer as a primary product or could be formed from styrene chemistry inside or outside of the printer. However, the decay of

the m/z 105 curve with $k = 5.5\ h^{-1}$ (obtained from a single exponential fit) is fast compared to the air exchange rate of $n = 1.5\ h^{-1}$, indicating styrene-ozone reactions in the chamber atmosphere. Further work is in progress.

Finally it should be mentioned that the measurement of formaldehyde, which is also a byproduct of styrene-ozone chemistry, by PTR-MS is not recommended in case of laser printer studies. The increasing humidity in the 1 m³ chamber from 10% to 80% during the printing process, which is due to the water content of the paper, might cause interferences [9, 10].

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On-line measurements of gaseous nitrated organic compounds in diesel vehicle exhaust by proton transfer reaction mass spectrometry

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Abstract

Gaseous nitrated organic compounds in diesel vehicle exhaust were analyzed on-line by means of a proton transfer reaction mass spectrometer and a chassis dynamometer. A diesel truck with an oxidation catalyst system was used as a test vehicle. Emissions of nitromethane; nitrophenol (NPh); C_7-, C_8-, C_9-, and C_{10}-nitrophenols; and nitrodihydroxybenzenes (NDHB) were observed in the diesel exhaust during the experiment under conditions of constant driving at 60 km h^{-1}. Time-resolved mass flow data of nitromethane, NPh, along with those of related volatile organic compounds (VOCs), were measured during a transient driving cycle. The patterns in mass flow variation of the nitrated organic compounds and other VOCs as a function of cycle time suggested that a possible precursor for nitromethane is acetone $(CH_3)_2CO$ formed in fuel combustion. In contrast, NPh originated from phenol C_6H_5OH which may be produced *via* the reaction of benzene C_6H_6 as a product of fuel combustion with OH radical.

Introduction

Diesel vehicle is an important part of the transportation sector because of their superior efficiency and high power output, while its exhaust is one of the largest contributors to environmental pollution problems. Combustion of diesel fuels brings about substantial emissions of nitrogen oxides (NO_x), volatile organic compounds (VOCs) and diesel exhaust particles (DEPs), and resulting in urban and regional haze and adverse health effects on humans. Furthermore, it has been recently reported that the secondary production of nitrated organic compounds such as nitro-PAHs, which are included in DEPs, can occur during catalytic exhaust gas treatment used to reduce NO_x, VOCs and DEPs [1]. In order to develop more efficient and harmless exhaust gas treatment, detailed relationship between emission characteristics of nitrated organic compounds and driving conditions should be understood. Here we perform on-line measurements of gaseous nitrated organic compounds in diesel vehicle exhaust and estimate those emission factors depending upon various driving conditions, by using proton transfer reaction mass spectrometry.

Experimental Methods

Figure 1 shows a schematic illustration of the chassis dynamometer system and method for sampling the diluted exhaust gas used here. A light-duty truck equipped with an oxidation catalyst system for aftertreatment was used in this study. The exhaust gas from the vehicle was analyzed on the chassis dynamometer system with a constant volume sampler (CSV, DLT-1860, Horiba) at

National Traffic Safety and Environment Laboratory. The total flow at the dilution tunnel was kept at 40 m^3 min^{-1}, and the exhaust gas was diluted by a factor of 56 (on average) with high-efficiency particulate air and charcoal-filtered air, which was controlled at 298 K temperature and 50 % relative humidity. The vehicle was set on the chassis dynamometer and driven either constantly at 60 km h^{-1} or according to the JE05 transient cycle. For the JE05 cycle, the vehicle was warmed by means of a preconditioning cycle before the measurement.Various non-methane volatile organic compounds (NMVOCs) in the exhaust gas were analyzed by using a commercial PTR-QMS utilizing H_3O^+ as a reactant ion (Ionicon Analytik GmbH). Mixing ratios of regulated substances CO and NO_x, greenhouse gases CH_4 and N_2O, and nitrogen dioxide NO_2 were measured by using the CVS instrument (MEXA-9000, Horiba), a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS-C, Aerodyne Research), and a cavity attenuated phase shift NO_2 monitor (CAPS-NO_2, Aerodyne Research), respectively.

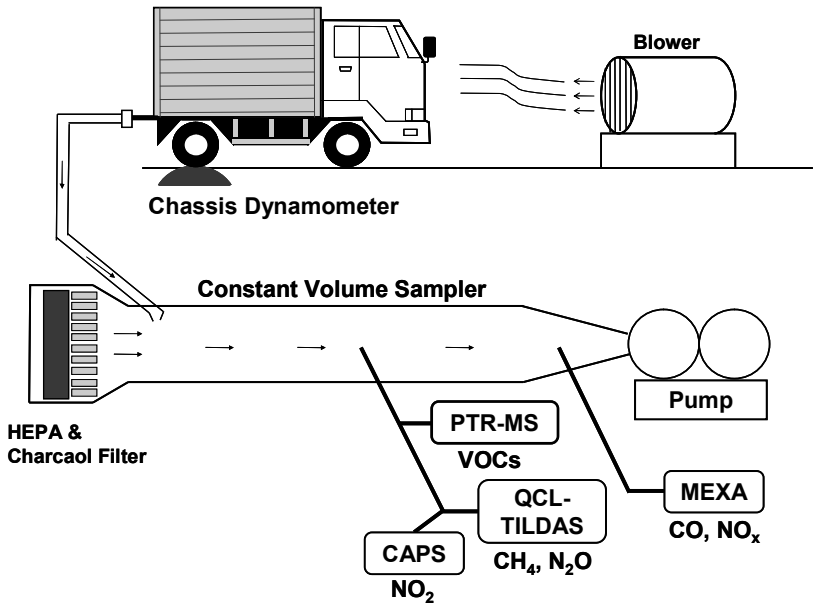

Figure 1: A schematic illustration of the constant volume sampler (CSV) and method for sampling the diluted exhaust gas.

Results and discussion

The PTR mass spectrum obtained under conditions of constant driving at 60 km h^{-1} (Fig. 2a) exhibited many signals attributable to a series of alkenes and/or unsaturated aldehydes/ketones at *m/z* 43+14*n*, saturated aldehydes/ketones at *m/z* 31+14*n*, carboxylic acids at *m/z* 47+14*n*, dienes at *m/z* 55+14*n*, aromatics at *m/z* 79+14*n*, dicarboxylic acids at *m/z* 91+14*n*, and alcohols at *m/z* 31, 95, and 109+14*n* ($n \geq 0$). To identify the nitrogen-containing compounds among the ion signals in the spectrum, the signal intensity ratio of a compound M at *m/z* 2*m* (even) to that at *m/z* 2*m*-1

nitrogen-containing compounds at *m/z* 2*m* and the ion signals at *m/z* 2*m* are attributed only to ^{13}C isotopologue signals of the compounds at *m/z* 2*m*-1, the I_{even} / I_{odd} ratios should be in the range of 0.01 to 0.17, depending on the number of carbons from C_1 to C_{16}. In contrast, high intensity ratios at *m/z* 2*m* suggest that there are substantial contributions from not only the ^{13}C isotopologue contributions of the compound at *m/z* 2*m*-1 but the nitrogen-containing compounds. The ion signals at *m/z* 2*m* with high intensity ratios can be assigned as follows: protonated acetonitrile ($CH_3CN \cdot H^+$ at *m/z* 42), nitrogen dioxide ion which is a fragment from alkyl nitrates (NO_2^+ at *m/z* 46), protonated acrylonitrile ($C_2H_3CN \cdot H^+$ at *m/z* 54), protonated nitromethane ($CH_3NO_2 \cdot H^+$ at *m/z* 62), protonated methyl nitrate ($CH_3ONO_2 \cdot H^+$ at *m/z* 78), protonated ethyl nitrate ($C_2H_5ONO_2 \cdot H^+$ at *m/z* 92), protonated nitrophenols (NPh $\cdot H^+$ at *m/z* 140), C_7-, C_8-, C_9-, and C_{10}-nitrophenols ($C_{7\text{-}10}$-NPhs $\cdot H^+$ at *m/z* 154+14*n*, $0 \le n \le 4$), and protonated nitrodihydroxybenzenes (NDHB $\cdot H^+$ at *m/z* 156) including 4-nitrocatechol. These results indicate the presence of nitrated organic compounds such as nitromethane, NPhs and NDHB in the diesel vehicle exhaust along with aromatics and oxygenated VOCs.

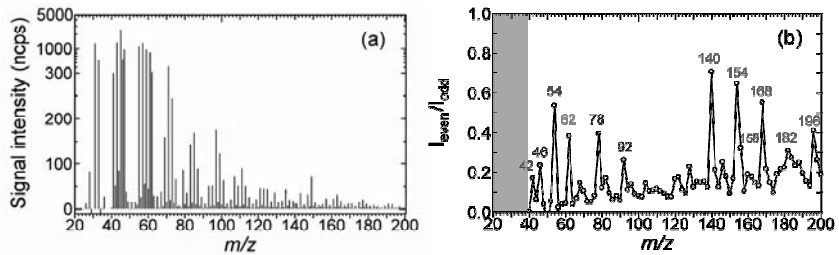

Figure 2. (a) Proton transfer reaction mass spectrum of diesel vehicle exhaust under conditions of constant driving at 60 km h^{-1}*: series of alkenes and/or unsaturated aldehydes/ketones, saturated aldehydes/ketones, carboxylic acids, dienes, aromatics, dicarboxylic acids, and alcohols. (b) Signal intensity ratio of M at* m/z *2*m *(even) to M at* m/z *2*m*-1 (odd),* I_{even} / I_{odd}*, as a function of* m/z *value.*

To investigate the dependence of driving conditions on emission factors of nitrated organic compounds, time-resolved mass flow data of nitrated organic compounds, along with those of related VOCs, were measured during a transient JE05 driving cycle including urban and highway driving. Figure 3 shows the time-resolved mass flows (mg s^{-1}) of (a) nitromethane (*m/z* 62) and (b) nitrophenols NPhs (*m/z* 140) obtained under hot and cold start conditions and velocity profiles (km h^{-1}) during the JE05 transient cycle. Both the nitrated organic compounds were emitted below 0.05 mg s^{-1} at any time under hot start conditions. The cold start emissions during the first 600 s of driving (0 – 600 s) were higher than hot start emissions, while in the case of the residual cycle times (600 – 1830 s), the emissions were similar for hot and cold starts. The increase in exhaust gas emission during initial phase of cold start driving is due in large part to poor ignition conditions in cylinder because of low engine and catalyst temperatures. On the basis of the time-resolved emissions data as shown in Fig. 3, various emission characteristics of the nitrated organic compounds, i.e., cold start extra emission (mg $start^{-1}$) and emission factors (mg km^{-1}) depending upon vehicle speed and acceleration, were deduced. The time-resolved measurements revealed that nitromethane emission was strongly correlated with emissions of CO, benzene, and

acetone, which are produced relatively quickly during acceleration, and these emissions appeared as sharp peaks. In contrast, NPh emission was moderately correlated with emissions of acetonitrile, acetic acid, and phenol, which exhibited broad peaks. These results suggest that a possible precursor for CH_3NO_2 is acetone $(CH_3)_2CO$ formed in fuel combustion. In contrast, NPh originated from phenol C_6H_5OH which may be produced *via* the reaction of benzene C_6H_6 as a product of fuel combustion with OH radical.

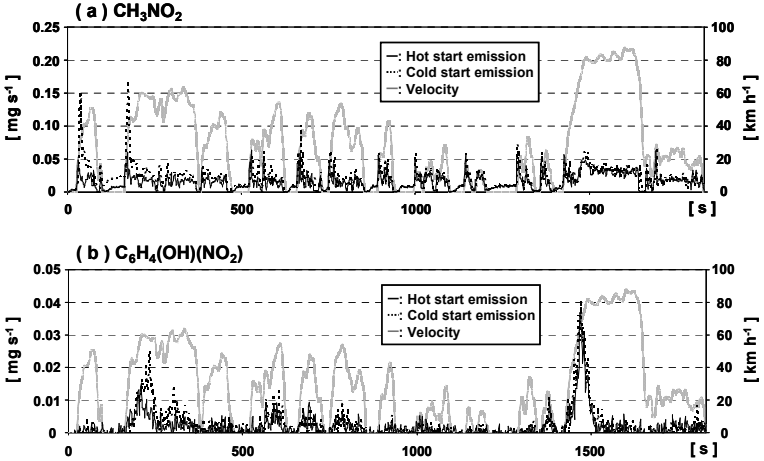

Figure 3: Time-resolved mass flows (mg s^{-1}) of (a) nitromethane (m/z 62) and (b) nitrophenols (m/z 140) obtained under hot and cold start conditions and velocity profiles (km h^{-1}) during the JE05 transient cycle. Solid black line: hot start emission; Dashed black line: cold start emission; Grey line: velocity.

Acknowledgement

The authors are grateful to the staff of National Traffic and Environment Laboratory for operation of the chassis dynamometer system. This work was financial supported by the Ministry of the Environment through the Environmental Technology Development Fund (S2-05 and S2-06 (FY 2009-2011)).

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Airborne Measurements Near the Deepwater Horizon Oil Spill

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Abstract

A NOAA WP-3D research aircraft made airborne measurements of the gaseous and aerosol composition of air over the Deepwater Horizon (DWH) oil spill that occurred in April-August of 2010 in the Gulf of Mexico. A narrow plume of hydrocarbons was observed downwind from DWH that is attributed to the evaporation of fresh oil on the sea surface. Mixing ratios of up to 10 ppbv of compounds such as the C9-aromatics were observed in this plume.

A mass spectrum was measured inside the narrow VOC plume showing a large number of peaks. Using laboratory measurements we show that the main peaks in the atmospheric spectrum are caused by the main constituents of crude oil: alkanes, cycloalkane, and aromatics.

We also determined the atmospheric fluxes of VOCs and used the oil composition data to derive the leak rate of crude oil for the flight days.

A much wider plume with high concentrations (>25 mg m^{-3}) of organic aerosol (OA) was attributed to secondary (SOA) formation from unmeasured, less volatile hydrocarbons that were emitted from a wider area around DWH. These observations provide direct and compelling evidence for the importance of formation of SOA from less volatile hydrocarbons.

Introduction

On April 20, 2010, the Deepwater Horizon (DWH) offshore drilling unit exploded, causing the riser pipe to rupture and crude oil to flow into the Gulf of Mexico from a depth of ~1500 meters. The oil leak rate was estimated to be 68,000 barrels per day making this one of the largest marine oil spills in history. On June 8 and 10, a NOAA WP-3D research aircraft, equipped with a large number of instruments to characterize trace gases and aerosol, performed two research flights on June 08 and 10, 2010 near DWH to explore the atmospheric impacts of the spilled oil and the clean-up activities.

Results

PTR-MS measurements of the evaporating spilled crude oil

The flight track of the NOAA WP-3 aircraft is shown in Figure 1 together with the extend of the spilled oil on the ocean surface. VOCs are evaporating from the freshly spilled oil forming a narrow plume downwind of the spill site, which can be seen in Figure 2B, where the flight track of the WP-3 is color-coded with the C9-aromatics.

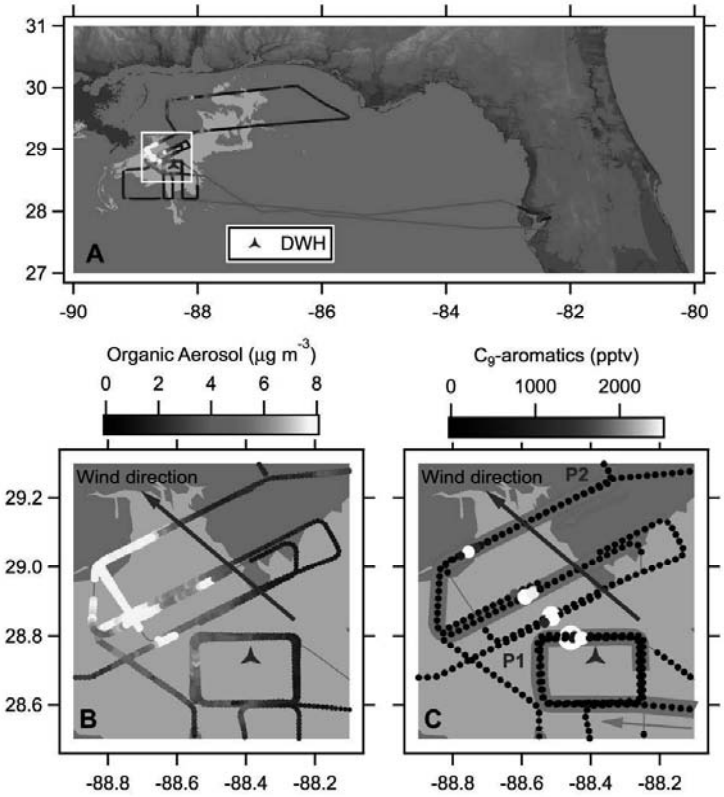

Figure 1: (A) Flight track on June 10, 2010, with data points below 900m color- and size-coded by the measured concentration of C_9-aromatics. The grey area underlying the flight track represents the extent of the oil slick derived from multiple satellite observations. The area indicated by the white square in panel A is shown in more detail in panel B and C color- and size-coded by the measured C9-aromatics and OA.

A PTR-MS mass spectrum, shown in Figure 2, was taken inside this narrow plume. Crude oil consists mainly of alkanes (detected on mass 43, 57, 71 and 8), cycloalkanes (mass 69, 83, 97, 111 and 125) and aromatics (mass 79, 93, 107, 121, and 135). To identify these major components in the atmospheric mass spectrum we used laboratory measurements of crude oil samples and analyzed them with GC-PTR-MS.

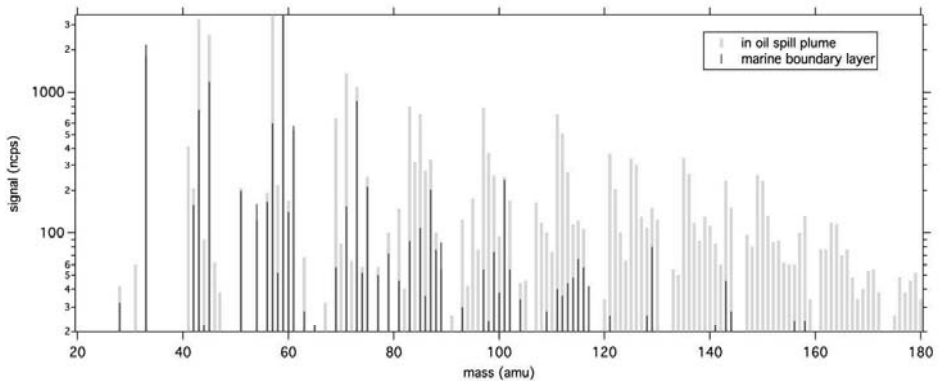

Figure 2: PTR-MS mass spectrum taken close to the DWH spill site in the narrow VOC plume.

Evaporative emissions constrain the oil spill rate

Using plume crossings by the WP-3D aircraft, the atmospheric fluxes of insoluble and volatile hydrocarbons including many aromatic compounds were determined. The fluxes are proportional to steady-state oil flow rates into the water. Therefore, the VOC fluxes from evaporation of fresh oil, coupled with reservoir fluid composition data, was used to estimate the amount of oil flowing into the water from the ruptured wellhead. The mass fluxes of individual VOCs are linearly related to their respective weight fraction in the reservoir fluid. The slope of this linear relationship gives the oil flow rate directly.

Organic aerosol formation downwind from the Deepwater Horizon oil spill

Aromatics and alkanes larger than C8 are known to be SOA precursors and were measured at very high mixing ratios downwind from DWH, higher than typically observed in urban areas. However, the SOA was not formed from these VOCs as the observed organic aerosol plume was much wider than the VOC plume. Instead, we argue here that IVOCs evaporating from the oil were the SOA precursors. As the evaporation is slower, these species were transported on the surface away from the area where the spilled oil surfaced, and were released to the atmosphere from a wider area (Fig. 3A). Further evidence for this conceptual model is obtained from the plume widths of the measured VOCs, whose vapor pressures span about two orders of magnitude. Figure 3B shows that close to DWH, the width of the VOC plume increased significantly with the molecular weight of the VOC.

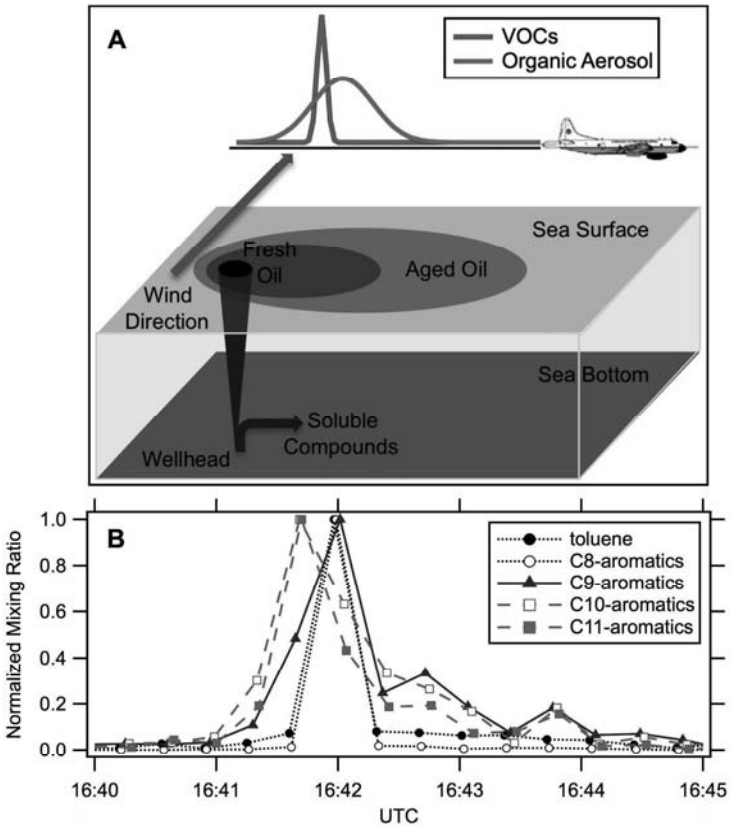

Figure 3: Conceptual model describing the observations of VOCs and organic aerosol downwind from the oil spill. Oil from the leaking riser pipe surfaces in a relatively small area. The most volatile fraction of the oil evaporates within hours, leading to a narrow atmospheric plume of VOCs downwind from the spill site. The less volatile fraction takes longer to evaporate, during which time the oil spreads over a larger area. Organic aerosol is formed from the less volatile fraction and is observed in a wider plume downwind. (B) Measurements of different aromatic species shortly downwind from the oil spill demonstrate that the plume broadens as a function of decreasing volatility, in accordance with the conceptual model.

The reaction of ozone at the air-human body interface

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Abstract

The skin's surface lipids are the human body's first line of defense against oxidizing agents in air. To investigate the products of the heterogeneous reaction of ozone, a powerful airborne oxidant, and human skin lipids we performed a series of *in vitro* and *in vivo* experiments using PTR-MS/PTR-TOF-MS as the analytical technique. The major volatile reaction products were acetone, 6-methyl-5-hepten-2-one, 2,6-dimethyl-2,6-undecadien-10-one (geranyl acetone) and decanal. Reaction products also included bifunctional compounds that contain carbonyl, carboxyl, or α-hydroxy ketone groups. Among these, four dicarbonyls have been identified: 4-oxopentanal; 1,4-butanedial; 4-methyl-8-oxo-4-nonenal; and 4-methyl-4-octene-1,8-dial. The results are fully consistent with the Criegee mechanism for ozone reacting with squalene, the major scavenger of ozone at the interface between air and the human envelope, and several unsaturated fatty acid moieties in their free or esterified forms. Reactions between ozone and human skin lipids were found to reduce the mixing ratio of ozone in air surrounding the human body, but concomitantly increase the mixing ratios of volatile by-products in the human breathing zone. Some of these products, especially the dicarbonyls, are respiratory irritants and may constitute an overlooked factor in the negative health effects associated with exposure to ozone.

Transient behavior of VOCs and particle emission from diesel engine equipped with diesel particulate filter

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Abstract

Diesel particulate filters (DPFs) have begun to be equipped to diesel engines in order to reduce particle emission from modern diesel engine for automobiles. DPFs are also effective to reduce VOCs (Volatile Organic Compounds) emission as well as fine particles. In normal operating condition, VOC and particle emissions are very low. But DPF must be regenerated periodically to burn stored particles. During the regeneration of DPF, nanoparticles are known to be formed downstream of DPF. VOCs emissions during regeneration and non-regeneration were measured by PTR-TOFMS and correlation of VOC and particle emissions was investigated. The results suggest that nucleation was caused not by organic compounds rather by inorganic compounds such as sulfate.

Introduction

Emissions from modern diesel engine for automobiles were significantly reduced by progress in combustion technology and emission after treatment devices. In order to reduce fine particle emission, diesel particulate filters (DPFs) have begun to be equipped to diesel engines. DPFs are very effective to reduce fine particles both in number and mass. DPFs are also effective to reduce VOCs (Volatile Organic Compounds) emission significantly. But capacity of DPF to store particles is limited, so DPF must be regenerated periodically to burn stored particles.

During such regeneration, nanoparticles are known to be formed downstream of DPF. VOCs emission during regeneration is of interest in view of toxicity and formation mechanism of nanoparticles.

Experimental Methods

In this work, a HD diesel engine equipped with DPF was investigated by two instruments capable of transient measurements (Fig.1). To measure particle emission, EEPS (Engine Exhaust Particle Sizer) was used to measure particle size distribution in the range between 5 and 500 nm. To measure VOCs, on-line mass spectrometer, PTR-TOFMS (Proton transfer reaction – Time of flight mass spectrometer), was used to measure several VOCs, such as benzene, toluene, acetaldehyde and 1,3-butadiene, which can detect at very low concentration as low as several ppb.

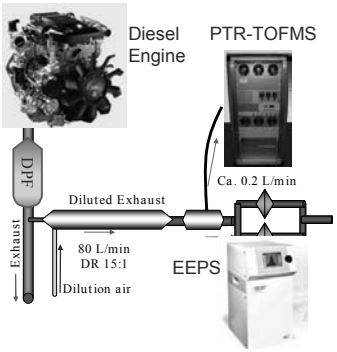

Figure 1: Experimental setup

Results and Discussion

During non-regeneration the DFP effectively reduces fine particles higher than 99.9% by number, with similar particle size distribution to that of engine-out. Several VOCs were undetectable by PTR-TOFMS, which means DPF also reduced VOCs effectively.

During active regeneration of DPF, fine particle emission increased with nanoparticle formation by nucleation. (Fig.2) Particle size distribution showed clear nucleation mode with mode diameter ca. 10 nm.

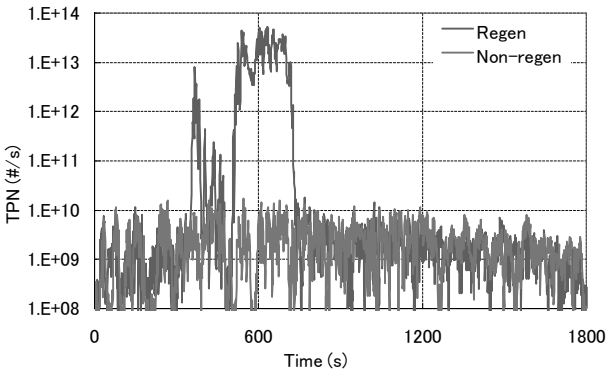

Figure 2: Comparison of total particle numbers between non-regeneration and regeneration

Simultaneous VOCs measurement showed that VOCs as well as THC emission increased prior to nucleation of particles then after reduced gradually. (Fig.4) It is suggested that nucleation was caused not by organic compounds rather by inorganic compounds such as sulfate.

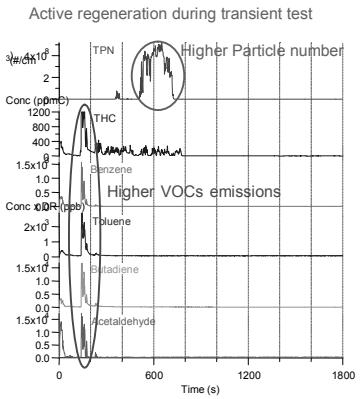

Figure 3: VOCs and THC emission during regeneration

Instruments & Technology and Future Trends

Mass Spectrometry of Atmospheric Aerosol: 1 nanometer to 1 micron

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Abstract

These projects apply mass spectrometric techniques to understand molecular composition and processing underlying the aerosol life cycle from nm to micron scales in the atmosphere.

Introduction

Despite much effort in the past decade, uncertainties in both climate impacts and health effects of atmospheric aerosols are still significant. During the last ten years, the application of mass spectrometry has enabled measurement of sub-micron chemical composition worldwide [1]; more recently the composition of atmospheric ions and cluster ions [2,3]; and most recently CIMS detection of organic acids from collected aerosol particles [4].

Experimental Methods

Starting with the development of the aerosol mass spectrometer in 2000 [5], mass spectra of size resolved, vaporized (at 600C) aerosol has shown that sub-micron aerosol chemical composition is roughly 50:50 inorganinc and organic worldwide [1]. Application of moderately high resolution ToFMS (Tofwerk) provides elemental analysis (C, H, O, N) of organics [6]. Factorization of complex organic mass spectra [1], combined with thermal denuder separation [7], has separated primary and secondary aerosol organic and shown that organics are highly oxidized on a time scale of days, with low volatility oxidized organic dominating remote aerosol organic [1].

By coupling the ToFMS directly to high pressure using two differentially pumped quadrupole ion guides, an atmospheric pressure interface (APi-ToF) has sampled ion directly from atmospheric pressure, with ion sampling/detection efficiencies of order 0.1-0.5%, up to 3000-4000 Th [2]. Ambient sampling in a boreal forest environment has distinguished the atmospheric production (from background cosmic rays and radon decay ionization) of inorganic and organic anions; positive ions are dominated by amine and pyridine species [3]. Recently, at the CLOUD (Cosmics Leaving OUtdoor Droplets) experiment CERN, the APiTOF has observed the appearance and growth of HSO4- anion clustered with up to 30 H2SO4 and 30 NH3 molecules, correlated with ion-induced nucleation of nano-particles, >2nm diameter.

Most recently, we have coupled the APi-ToFMS to the MOVI-CIMS technique developed at the University of Washington [4]. Gas and aerosol composition are alternately analyzed using high pressure CIMS (~100 mbar), typically using the C3H7O- reagent ion. Vapor composition is detected directly while sub-micron aerosol is collected on a multiple-orifice-vaporization-impactor; subsequent thermal desorption of the aerosol component provides volatility resolved

aerosol composition. Organic acids are detected with very high sensitivity (up to 1ppt/hz, unpublished results, UC San Diego).

Results

Detected ambient anions in Hyytiälä, a forest station in central Finland, resolve daytime and nighttime abundance of inorganic (sulfate, nitrate-containing) anion clusters and organic anions (up to 500 Th), respectively. Positive mass defects indicate organics are highly oxidized (O/C elemental ratio ~1) very similar to LV-OOA secondary organic factors observed with the ToF-AMS [1,3]. In fact, organic anions can be chemically related to oxalic acid, the simplest dicarboxylic acid. Another key observation in Hyytiälä is that the HSO4-(H2SO4)3 anion is observed as a cluster with NH3. This can be compared to observations in the CLOUD experiment where at 20C all HSO4-(H2SO4)n clusters with n>2 have contain NH3 or alkyl amine molecules.

Measurements of aerosol composition with the MOVI-CIMS have observed high molecular weight organic anions (up to 500 Th), bridging the gap between APi-ToF observation of organic anions in the gas phase and AMS observation of highly oxidized organics condensed in sub-micron aerosol. Thermal volatility decreases with increasing molecular weight. On-going work is characterizing sensitivity, selectivity and thermal decomposition during vaporization complex organics in collected aerosol.

Discussion

The ultimate goal of these mass spectrometric studies is provide a comprehensive picture of the molecular composition and evolution of aerosol particles, from nm to micron scales. The AMS provides fast, continuous of measure of size resolved, elemental composition of sub-micron aerosol. The APi-ToF provides a direct measure of ambient ion chemistry, kinetically controlled by short atmospheric ion lifetimes (minutes); this is particularly powerful for observing the growth of clusters during nucleation events. MOVI aerosol collection uses more conventional CIMS analysis to monitor parent ions from organic mixtures, limited by the capability of vaporizing low volatility compounds. Extension to other reagent ion chemistries (including positive ion PTRMS) hold promise for complete characterization of these complex systems, both for aerosol components and their gas phase precursors.

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Experiences at the Fondazione Edmund Mach with PTR-ToF-MS data: from analysis of mass spectra to chemometrics and data mining

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Abstract

About one year ago, at FEM, we started applying the PTR-ToF-MS instrument in food science and technology. While several advantages of PTR-ToF-MS with respect to its quadrupole based precursor were immediately evident, as, for instance, the higher mass resolution and range, it turned out that its main, perhaps even the only, drawback was related to the increased size and complexity of the data sets obtained. It appears that this is the main limitation to its full use and widespread application. With this contribution, we would like, on one hand, to describe our solutions to some issues which arise when dealing with PTR-TOF-MS data. This also aims at helping other laboratories that are probably facing the same problems. On the other hand, we would like to stimulate/initiate the discussion on this complex and intriguing aspect of PTR-MS technology.

The issues that we were forced to address during our initial work with PTR-ToF-MS data and which we would like to discuss in this contribution are:

- Spectra handling and peak alignment. In this exploratory phase, we considered the handling of the HDF5 files which are commonly used to store TOF spectra, by Matlab capabilities. Data pre-processing issues were also considered. We propose a procedure of how to construct the spectra baseline and how to improve the signal-to-noise ratio without distorting the spectra. Peak alignment and dead time correction were also addressed. In particular, we achieved a satisfactory mass accuracy for sum formula determination in most cases [1] and demonstrated the possibility to extend the ToF dynamic range [2].
- Peak Extraction. A complete methodology for the automatic generation of a peak intensity matrix from an arbitrary number of samples is proposed. The procedure includes an automatic peak finding procedure based on a new algorithm [3]. A key aspect we considered is the possibility to work with a peak shape extracted directly from the spectra, instead of employing Gaussians, modified Gaussians or other functions to approximate the peaks. The methodology proved to be successful for several applications in food science, for example in cheese sample classifications [4] and in monitoring lactic fermentation [5].

- Data visualisation and exploration. The information contained in the result matrix can be explored and visualised by unsupervised statistical methods, such as principal component analysis (PCA), which is often suitable for a preliminary data evaluation [3].
- Chemometrics and data mining. The proper development of optimal classification or calibration models, in general, may require more sophisticated methods than unsupervised methods. We applied several multivariate and data mining supervised classification methods, such as Random Forest (RF), Penalized Discriminant Analysis (PDA), Discriminant Partial Least Squares (PLS) and Support Vector Machines (SVM), all of which have already been successfully applied to PTR-Quad-MS data[3].
- Feature extraction. If an efficient classification model is available, it is always important to know which peaks contribute most to the separation of the different classes. An efficient way to do this is to use an appropriate feature selection method, as for example Random Forest - Recursive Feature Elimination (RF-RFE), introduced by Granitto et al. [6]. RF-RFE can identify the most relevant peaks in a multivariate and collinear data matrix, even in situations when the number of samples is much lower than the number of measured peaks. We applied RF-RFE to PTR-ToF-MS data and compared it with other feature selection approaches, such as the standard analysis of variance.

In summary, PTR-ToF-MS generates huge amount of data in a very short time, but nevertheless appears to be quite suitable, e.g. for high throughput applications, or long processes monitoring with high time resolution. In order to fully exploit the data sets that PTR-ToF-MS is generating, a simple data analysis is not sufficient in all cases, and suitable and automatic procedures must be set up. We implemented here dedicated software to support all phases of data analysis from the handling and analysis of the spectra all the way to data mining and tested them with concrete problems in food science and technology.

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PTR-MS and Saturated Alcohols: effects on product ion distributions of hollow cathode and drift tube operating conditions

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Abstract

Proton transfer reaction mass spectrometry (PTR-MS) has grown in recent years into a versatile tool for trace gas analysis and monitoring. To aid in the development of PTR-MS as an analytical and monitoring tool the full implication of the operating conditions of the mass spectrometer must be analysed and understood.

This study looks at the effect of changing operating parameters for a series of saturated alcohols. The operating parameters focussed on are those affecting the drift tube and the hollow cathode ion source. Branching ratios are presented that show substantial dependence on the operating conditions of the drift tube, and for the first time the hollow cathode ion source.[1]

Introduction

Many saturated alcohols can be detected in breath analysis or microbial studies due to their importance in metabolic processes of both animals and microbes. Saturated alcohols are also of importance as exhaust by-products of manufacturing and chemical processes in industry and the wider environment. The series of saturated alcohols investigated ranged from methyl to hexyl compounds. A full list is given in Table 1. Previous studies have examined saturated alcohols,[2, 3] but not with consideration to the ion source operating conditions.

It is often claimed in PTR-MS literature that by knowledge of a compound's fragmentation pattern (branching ratio) the compound can be identified.[4] Although the introduction of PTR-TOF-MS technology has made compound identification more reliable a well understood fragmentation pattern is still an important aid to reliable compound identification.[5] This study hopes to improve the reliability of compound identifications made by PTR-MS by fully studying how the ion molecule reactions occurring in the drift tube depend on PTR-MS operating parameters.

Since the earliest studies of ion-molecule reactions using drift tube technology, the drift field, and temperature and pressure of the drift region has been considered centrally important to the observed product ion distribution.[6] The effect of altering the source of reagent ions has been so far largely overlooked in literature. When ions are not sufficiently thermalized in the drift tube the operating conditions of the ion source can have a substantial effect on the observed fragmentation pattern.

Chemical Name (Proton affinity/ kJmol^{-1})	Chemical Formula
Methanol (754.3)	CH_3OH
Ethanol (776.4)	C_2H_5OH
1-Propanol (786.5)	C_3H_7OH
Iso-propanol (793.0)	C_3H_7OH
1-Butanol (789.2)	C_4H_9OH
Iso-butanol (793.7)	C_4H_9OH
Tertiary Butanol (802.6)	C_4H_9OH
2-Butanol (815)	C_4H_9OH
Cyclopentanol	$C_5H_{10}O$
1-Pentanol	$C_5H_{11}OH$
Cyclohexanol	$C_6H_{12}O$
1-Hexanol	$C_6H_{13}OH$
3,3, Dimethyl-2-butanol	$C_6H_{13}OH$

Table 1: List of saturated alcohols studied.

Experimental Methods

Each compound in this experiment was analysed using a proton transfer reaction quadrupole mass spectrometer, with hollow cathode ion source and drift tube. Each sample was introduced to the instrument, as outlined in Figure 1. A few drops of sample were placed onto a piece of cotton wool inside the barrel of a disposable 10 ml syringe. By connecting the syringe to an inlet flow of scrubbed nitrogen the vapour could be introduced at a controllable rate by adjusting the pump rate of the syringe drive. With an adjustable concentration, any concentration dependence could be analysed and extrapolated to trace concentration. All waste sample gasses were vented to external atmosphere.

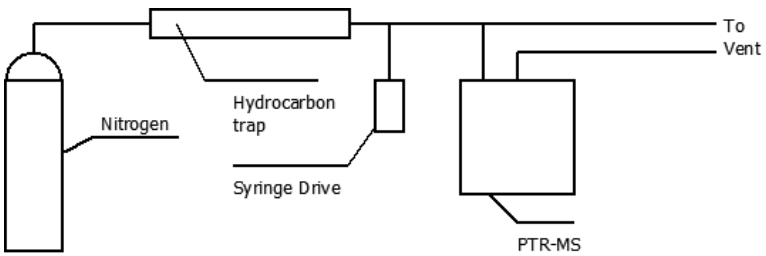

Figure 1. Experimental set-up used to explore the branching ratio of a series of saturated alcohols.

The drift tube was controlled by an electronic thermostat and pressure controller to 43º C and 2.06 mbar. The drift field was adjusted between 400-600 V in steps of 20 V, this provided a reduced electric field (E/N) range of between 92-138 Td with approximately 5 Td intervals. The current and voltage of the hollow cathode could both be adjusted, it was decided to keep the voltage constant at 600 V and adjust the current. With a 600 V voltage the current could be adjusted between 10 mA and 2 mA in steps of 0.5 mA without the reagent ion signal becoming unstable.

Results

The reactions of H_3O^+ reagent ions with saturated alcohols that occurred within the drift tube environment showed predominantly dissociative behaviour. The product ion branching ratios were found to be very dependent on the value of the reduced electric field (E/N) applied in the drift tube. With fixed drift tube conditions, differences were observed in product ion distributions where the operating current of the hollow cathode was changed. An example of the data taken is shown in Figure 2 where the product ion branching ratio for iso-propanol is seen to depend strongly on both drift tube and hollow cathode operating conditions.

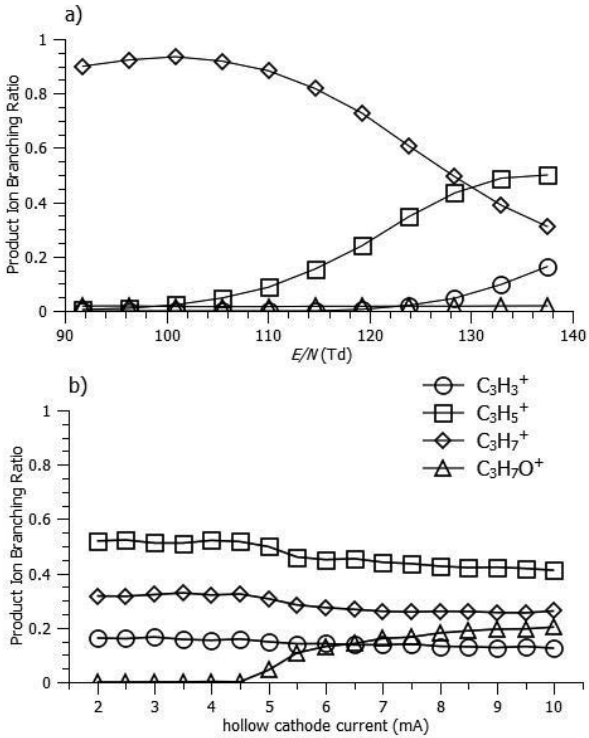

Figure 2. The product ion branching ratio of iso-propanol is shown as a function of a) reduced electric field (5 mA operating current) and b) as a function of hollow cathode emission current (138 Td reduced electric field).

Discussion

Changes in the product ion branching ratios observed from changes in the hollow cathode emission current are attributed to changes in the internal energy distribution within the reagent ions. An understanding and determination of the internal energy distribution of the reagent ions is therefore considered to be important if PTR-MS instrumentation is to be correctly characterized. A fuller consideration of the operating conditions of PTR-MS must be considered to gain a fuller understanding of the drift tube reactions used in PTR-MS.

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PTR-MS filter test device of toxic substances

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Abstract

The focus of this presentation is to demonstrate a novel filter test rig for adsorption tests with highly toxic substances in the context of the actual research project ZF³ (Center for filtration research and functionalized surfaces).

Within this research project the Institute of Energy and Environmental Technology e.V. (IUTA) has developed a new filter test rig which enables the investigation of the adsorption of toxic gases in the sub-ppm concentration range. The concentration of TIC and TIM (Toxic Industrial Chemicals, Toxic Industrial Materials) will be measured with two new Compact-PTR-MS (Proton Transfer Reaction – Mass Spectrometry) arranged as a new filter test system including a gas calibration unit (GCU). The filter efficiency of different kinds of adsorbing or catalytically effective filter systems can be measured with single gases or a mixture of them.

The measuring performances will be presented as well as the actual research project ZF³, the developed new filter test rig and its PTR-MS measurement system along with some results.

Introduction

For several years, the Institute of Energy and Environmental Technology e.V. (IUTA) in Duisburg, Germany, is conducting measurements on the gas and odor removal efficiency of filtration media within research projects, funded by public bodies and industry.

The filter test center of IUTA contains several filter test rigs for studies of the performance of filter media by measuring the particle and gas reduction. IUTA tests different kinds of filter systems in the field of cabin air systems, compressed air systems and air condition systems. The filter efficiencies are specified here with tailored particles, gases or odors to arrange filter tests according to DIN 71460 (IS0 11155), ISO 8573 / ISO 12500, EN 779 or DIN EN 13725.

The ability of adsorbents to remove gaseous components from different carrier gases is evaluated by measuring the breakthrough curves. Concerning the group of adosorbates which are mainly used in cabin air filters, the substances are prescribed in guidelines. In DIN EN 71460 n-butane or toluene are proposed and they are measured by FID (flame ionization detector) down to a concentration of 1 ppm. On the other hand, in the field of the adsorption of highly toxic substances such as phosgene and further TIC and TIM (Toxic Industrial Chemicals, Toxic Industrial Materials) only a few institutes in Europe are able to handle these substances according to the appropriate guidelines. In Germany the adsorption measurements of highly toxic substances are carried out only in military institutions. The military applications require relatively high concentrations of those substances in the range of 1000 to 5000 ppm, while measuring the breakthrough curves. The application of toxic substances in the sub-ppm range outside the

military environment is growing and e.g. includes chemical intermediates like HCN or COCl2 and consumer-oriented products of HCN in almonds or cigarette smoke.

The gas and aerosol filter manufacturers have an ongoing strong need for new and innovative products in order to strengthen their market position. Functionalities based on new materials, combined features, inner & outer surface properties provided e.g. by nanotechnology or compact design will lead to a significant improvement in filter performance.

The center of filtration research and functionalized surfaces (ZF^3) at IUTA e.V. bundles the local know-how of several expert groups to functionalize surfaces and test their performance in view of particle and gas removal.

One aim of the developed functionalized surfaces is the realization of final products for applications in adsorptive systems (*see Figure 1*).

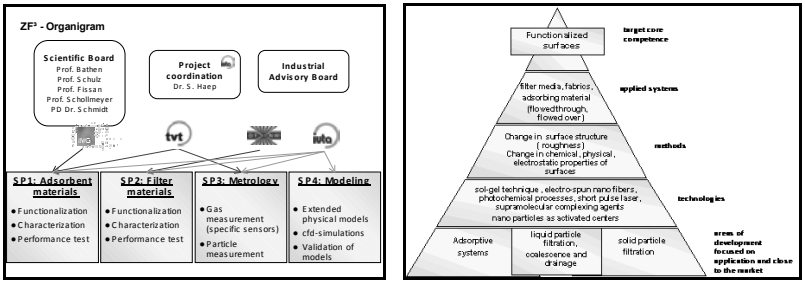
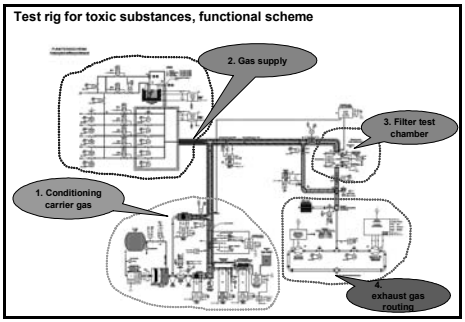


Figure 1: ZF^3 organigram and Top Down structure

Hence it is required to develop test procedures and test rigs that cover the field of adsorption tests with toxic substances in the sub-ppm range to take care of the TLV (threshold limit value), also and especially in view of the new European chemicals directive REACH (Registration, Evaluation, Authorization of Chemicals).

Filter test facility, PTR-MS-filter test system and first results

The new test rig was designed in a flow through setup which enables the investigation of the adsorption of toxic gases in the sub-ppm concentration range. The test rig has to fulfill certain requirements in particular with regard to leak tightness, material resistance and occupational safety. *Figure 2* shows a functional scheme of the test rig.



The carrier gas flow (air, synthetic air or nitrogen) will be conditioned in ranges up to 90 % relative humidity at temperatures from 10°C to 50°C (conditioning carrier gas) and mixed with the toxic substances up to the test concentrations of the adosorbates (gas supply). The decontamination process is enhanced via an additional vacuum system and directly connected to a thermal after-burning plant (exhaust gas routing). For decontamination the contaminated pipes of the system can be heated up to about 240°C.

The test concentrations conform to the TLV (threshold limit value) or the TRC (technical reference concentration). The total flow is adjustable in a range of 1 Nm³/h to 25 Nm³/h.

The investigation of the breakthrough curves (*see Figure 3*) of different adsorbing systems (flat media, foams, bulk layers, canisters) related to various toxic substances at different relative humidities will be carried out in this new filter test laboratory of IUTA.

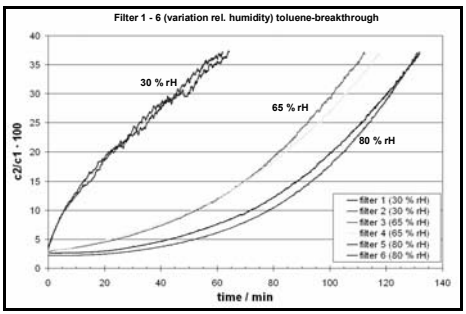


Figure 3: Breakthrough curves of toluene measured with FID

The new filter test device (*see Figure 4*) is equipped with two PTR-MS devices to measure the raw gas concentrations (P1) and the clean gas concentrations (P2) in the ppm-range up to 1000 ppm and in the ppb-range down to 5 ppb. This arrangement is very important for filter tests, because of measuring the initial breakthrough concentration from ppb levels up to 80 % breakthrough in the high ppm range.

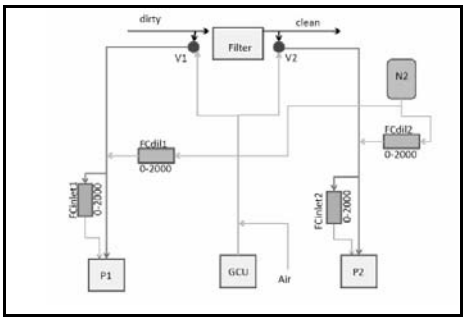


Figure 4: Filter test device with two PTR-MS and gas calibration unit (GCU)

Additionally two dilution systems are installed to establish the linear detection of high concentration levels in the raw gas (“dirty”) and the high breakthrough concentration in the clean gas area (“clean”). Both PTR-MS-Systems are equipped with the Switchable-Reagent-Ions (SRI)-function which is able to produce three kinds of primary ions with different ionisation energies:

This will enable measurements of a wide range of different test gases with different ionisation potentials as single components as well as a mixture of them.

The analysis system is completed with a gas calibration unit (GCU) which also allows calibrated measurements at different relative humidities (*see Figure 5*).

Figure 5: Test facility with two PTR-MS and one gas calibration unit (GCU)

First tests showed that the transmission data in the calibration tool have to be corrected, if the matrix of the gas mixture is measured at very different relative humidities (*see Figure 6*).

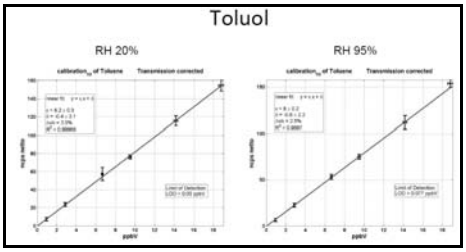


Figure 6: Detection of toluene at different relative humidities

That is noteworthy, because we intend to characterize the filter systems in a range from 10 % up to 90 % relative humidity.

Conclusions

One main focus of the project "Center for filtration research and functionalized surfaces ZF³" is on the improvement of filter media quality by functionalization of the adsorbing filter media.

The new filter test rig and its analytical PTR-MS-system will be able to carry out performance tests of different adsorbing systems (flat media, foams, bulk layers, canisters) with a large number of TIC and TIM. The new installed PTR-MS-system including its dilution system has a great advantage compared to the FID-measurement, because the new analysis system is able to measure concentrations from the high ppm concentration level down to the low ppb concentration level and to detect fragments at catalytically effective filter systems.

The evaluation of new filter systems can be carried out at different adjustable temperatures, relative humidities, volume flows and applied raw gas concentrations. First results especially in the field of improvement of the adsorption properties by functionalization of the adsorbing surface are expected in spring 2011 and will be presented at the conference.

H_3O^+, NO^+ and O_2^+ as precursor ions in PTR-MS: isomeric VOC compounds and reactions with different chemical groups

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Abstract

Most PTR-MS instruments employed so far use an ion source consisting of a hollow cathode discharge in water vapour which provides an intense source of protonated water (H_3O^+). However, the use of other ions, e.g. NO^+ and O_2^+, can be useful for the identification of VOCs, for separation of isomers and for the detection of VOCs with proton affinities below that of H_2O [1].

For certain chemical compound groups these different precursor ions show characteristic reaction paths and different product ions and especially charge transfer leads very often to different product ions for isomeric compounds.

Introduction

The different precursor ions (XH^+, X^+) produced in the hollow cathode enter the drift tube and react with the VOCs. The advantage of using different precursor ions lies in the fact that they may lead to different product ions allowing for better identification of the mass peaks. By using protonated water the precursor ion H_3O^+ is reacting with the VOC by transferring the proton, whereas in case of the NO^+ and the O_2^+ precursor ions one dominant reaction with the VOC is charge transfer, i.e.

$$XH^+ + AB \rightarrow ABH^+ + X$$

$$X^+ + AB \rightarrow AB^+ + X$$

If these reactions are exothermic it is possible to detect the products with a quadrupole mass spectrometer or a time of flight mass spectrometer. Only a few precursor ions are suitable for analyzing ambient air in a PTR-MS instrument. To reach low detection limits the precursor ion must be relatively nonreactive with the major air components N_2, O_2, H_2O, Ar and CO_2 [2]. The proton affinity of water is lower than that of nearly all organic compounds, many hydrocarbons, some anorganic compounds and is higher than the major air compounds. The ionization energy of oxygen is 12.06eV and therefore higher than the ionization energy of most of the compounds which protonated water can ionize [3]. The ionization energy of NO is just 9.26eV which is lower than the ionization energies of most organic compounds and hydrocarbons. With O_2^+ as precursor ion the energy transfer to the product is generally higher than in the case of H_3O^+ which results in

$$O_2^+ + AB \rightarrow A^+ + B + O_2$$

Moreover, by using NO^+ as precursor ion another reaction can occur if the heat of formation on the product side is lower than the heat of formation of the reactants.

$$NO^+ + ABH \rightarrow AB^+ + NOH$$

In most cases the ionization energy of NO is lower than that of the ABH and so it is not possible to see the ABH^+. At very low collision energies sometimes depending on the bonding energy three body clustering reactions can occur, i.e.

$$NO^+ + ABH + N_2 \rightarrow (NOH \cdot AB^+)^* + N_2 \rightarrow NOH \cdot AB^+ + N_2$$

The collision energy or the E/N ratio which is usually used at standard conditions in a PTR-MS is too high to see a significant amount of this cluster reaction but it is possible to decrease the drift voltage to measure these products.

Results

In general the main advantage of O_2^+ is to see compounds which are not measureable with protonated water. For example nearly all halogenated hydrocarbons are detectable with O_2^+ whereas just the very large ones and the aromatic halogenated compounds are detectable with H_3O^+.

halocarbons		H_3O^+		NO^+		O_2^+	
Name	formula	reaction	k	reaction	k	reaction	k
Methylclorid	CH_3Cl		-		-	CH_2Cl^+	k_C
Vinylchlorid	C_2H_3Cl		-		-	$C_2H_3Cl^+$	k_C
Ethylcloride	C_2H_5Cl		-		-	$C_2H_4Cl^+$	k_C
Methylenecloride	CH_2Cl_2		-		-	$CHCl_2^+$	k_C
Bromomethane	CH_3Br		-		-	CH_3Br^+	k_C
1,2 Dicloroethylene 1,1 Dicloroethylene	$C_2H_2Cl_2$ $C_2H_2Cl_2$	$C_2H_2Cl_2H^+$	k_C		-	$C_2H_2Cl_2^+$ $C_2H_2Cl_2^+$	k_C
1,2 Dicloroethane 1,3 Dicloroethane	$C_2H_4Cl_2$ $C_2H_4Cl_2$		-		-	$C_2H_3Cl_2^+$ $C_2H_3Cl_2^+$	k_C
t-1,3-dicloropropene c-1,3-dicloropropene	$C_3H_4Cl_2$ $C_3H_4Cl_2$		-		-	$C_3H_4Cl_2^+$ $C_3H_4Cl^+$ $C_3H_4Cl_2^+$ $C_3H_4Cl^+$	k_C
Clorobenzene	C_6H_5Cl	$C_6H_5ClH^+(100)$	k_C	$C_6H_5ClH^+(100)$	k_C	$C_6H_5Cl^+$	k_C
1,2-dicloropropane	$C_3H_6Cl_2$				-	$C_3H_5Cl_2^+$ $C_3H_6Cl^+$	k_C
Cloroform	$CHCl_3$				-	CCl_3^+	k_C
Diclorodifluoromethane	CF_2Cl_2				-	$CFCl_2^+$	k_C
Tricloroethylene	C_2HCl_3	$C_2HCl_3H^+(100)$	k_C		-	$C_2HCl_3^+$	k_C
1,1,1-tricloroethane 1,1,2-tricloroethane	$C_2H_3Cl_3$ $C_2H_3Cl_3$				-	$C_2H_2Cl_3^+$ $C_2H_2Cl_3^+$	k_C
1,1,2triclorofluromethane	$CFCl_3$				-	$CFCl_2^+$	k_C

						CCl_3^+	
1,2-diclorobenzene 1,3-diclorobenzene 1,4-diclorobenzene	$C_6H_4Cl_2$ $C_6H_4Cl_2$ $C_6H_4Cl_2$	$C_6H_4Cl_2H^+$(100)	k_C	$C_6H_4Cl_2H^+$(100)	k_C	$C_6H_4Cl_2^+$ $C_6H_4Cl_2^+$ $C_6H_4Cl_2^+$	k_C
Carbontetracloride	CCl_4				-	CCl_3^+	k_C
Tetracloroethylene	C_2Cl_4				-	$C_2Cl_4^+$	k_C
1,1,2,2-tetracloroethane	$C_2H_2Cl_4$				-	$C_2HCl_4^+$ $C_2H_2Cl_3^+$	k_C
1,2-diclorotetrafluroethane	$C_2Cl_2F_4$				-	$C_2ClF_4^+$ $C_2Cl_2F_3^+$	k_C
1,2,4-triclorobenzene	$C_6H_3Cl_3$	$C_6H_3Cl_3H^+$(100)	k_C	$C_6H_4Cl_2H^+$(100)	k_C	$C_6H_3Cl_3^+$	k_C
1,1,2-triclorotrifluroethane	$C_2Cl_3F_3$				-	$C_2Cl_3F_2^+$ $C_2Cl_2F_3^+$	k_C
Dibromoethane	CH_2Br_2				-	$C_2H_4Br^+$	k_C
Hexacloro1,3-butadiene	C_4Cl_6	$C_4Cl_6H^+$(100)	k_C		-	$C_4Cl_6^+$	k_C

Table 1: List of observed reactions of H_3O^+, NO^+ and O_2^+ with several halogenated hydrocarbons

By using NO^+ as precursor ion in nearly all cases the product ions are different from the product ion by using protonated water. Very often also isomeric compounds show different product ions. For instance, isomers like aldehydes and ketones or acids and esters show in many cases different product ions in the reaction with NO^+.

Aldehydes		H_3O^+		NO^+		O_2^+	
Name	formula	reaction	k	reaction	k	reaction	k
formaldehyde	HCHO	CH_3O^+ (100) + H_2O	k_C	--	$<<k_C$	products	k_C
acetaldehyde	CH_3CHO	$C_2H_5O^+$ (100) + H_2O	k_C	$C_2H_3O^+$ + HNO	$<k_C$	products	k_C
Acrolein	C_2H_3CHO	$C_3H_5O^+$ (100) + H_2O	k_C	$C_3H_3O^+$ + HNO	k_C	products	k_C
1-propanal	C_2H_5CHO	$C_3H_7O^+$ (95) + H_2O $C_2H_3O^+$ (5) + $2H_2O$	k_C	$C_3H_5O^+$ + HNO	k_C	products	k_C
crotonaldehyde	C_3H_5CHO	$C_4H_7O^+$ (100) + H_2O	k_C	$C_4H_5O^+$ + HNO	k_C	products	k_C
1-butanal	C_3H_7CHO	$C_4H_9O^+$ (30) + H_2O $C_3H_5O^+$ (70) + $2H_2O$	k_C	$C_4H_7O^+$ + HNO	k_C	products	k_C
valeraldehyde	C_4H_9CHO	$C_5H_{11}O^+$ (10) + H_2O $C_4H_7O^+$ (90) + $2H_2O$	k_C	$C_5H_9O^+$ + HNO	k_C	products	k_C
hexanal	$C_5H_{11}CHO$	$C_6H_{13}O^+$ (5) + H_2O $C_5H_9O^+$ (95) + $2H_2O$	k_C	$C_6H_{11}O^+$ +HNO	k_C	products	k_C
heptanal	$C_6H_{13}CHO$	$C_7H_{15}O^+$ (5) + H_2O $C_6H_{11}O^+$ (95) + $2H_2O$	k_C	$C_7H_{13}O^+$ +HNO	k_C	products	k_C
Octanal	$C_7H_{15}CHO$	$C_8H_{17}O^+$ (5) + H_2O $C_7H_{13}O^+$ (95) + $2H_2O$	k_C	$C_7H_{15}O^+$+HNO	k_C	products	k_C

nonanal	$C_8H_{17}CHO$	$C_9H_{19}O^+$ (5) + H_2O $C_8H_{15}O^+$ (95) + $2H_2O$	k_C	$C_9H_{17}O^+$ +HNO	k_C	products	k_C

Ketones		H_3O^+		NO^+		O_2^+	
Name	formula	reaction	k	reaction	k	reaction	k
Acetone	CH_3COCH_3	$C_3H_7O^+$ (100) + H_2O	k_C	$C_3H_6O^+$ +NO $C_3H_6ONO^+$	$<<k_C$ f(E)	products	k_C
1-butanone	$C_2H_5COCH_3$	$C_4H_9O^+$ (100) + H_2O	k_C	$C_4H_8O^+$+NO $C_3H_6ONO^+$	$<<k_C$ f(E)	products	k_C
3-pentanone	$C_2H_5COC_2H_5$	$C_5H_{11}O^+$ (100) + H_2O	k_C	$C_5H_{10}O^+$+NO $C_3H_6ONO^+$	$<<k_C$ f(E)	products	k_C
Hexanone	$C_2H_5COC_3H_7$	$C_6H_{13}O^+$ (100) + H_2O	k_C	$C_6H_{12}O^+$+NO $C_3H_6ONO^+$	$<<k_C$ f(E)	products	k_C
Heptanone	$C_2H_5COC_4H_9$	$C_7H_{15}O^+$ (100) + H_2O	k_C	$C_7H_{14}O^+$+NO $C_3H_6ONO^+$	$<<k_C$ f(E)	products	k_C

Table 2: List of observed reactions of H_3O^+, NO^+ and O_2^+ with various aldehydes and ketones

Acknowledgement

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Applications in Food Science

Food flavour analyses: traditional and new challenging methods

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Abstract

The sensory properties of food are important determinants in the choice of foodstuffs by the consumer, and flavour plays a prominent role, with clear links to consumer preferences. Flavour may be defined as the combination of taste and odour, sensations of pain, heat and cold (chemesthesis or trigeminal sensitivity), and tactile sensation. Even if sensory analysis allows the best description of flavour characteristics, only chemical analysis gives access to the individual compounds responsible for these characteristics. As aroma is known to have a major impact in the overall flavour, measuring flavour means primarily analyzing volatile compounds that are sensed in the nose at the olfactory receptors either *via* the orthonasal (odour) or retronasal (aroma) routes when foods are eaten. However, as no single extraction method yields an "accurate" picture of a food aroma, it appeared much more efficient to concentrate efforts on the identification of those compounds that are really relevant to the perceived flavour. Once an extraction method as representative as possible of the food flavour has been chosen [1], various methods of gas chromatography coupled to olfactometry (GC-O) have been commonly used in order to determine the key volatiles that contribute significantly to the flavour of the food (see [2] for a recent review). Some challenges concerning GC-O will be discussed.

As it is still not known how the various volatiles combine to produce an overall sensory impression, it is particularly difficult to predict an aroma perception on the basis of GC-O data only. Demanding recombination experiments have to be undertaken [3]. Therefore, specific instrumental techniques have been developed for the global analysis of food flavour. The methods currently used in quality control of food flavour are still usually based on sensory evaluation by a panel of experts. These panels are able to monitor the quality of a particular food, to detect defects and to compare samples for classification purposes. Nevertheless, obtaining faster results at lower cost using instruments could be an interesting alternative. The so-called 'electronic noses' based on gas sensor technology, despite some important drawbacks for some of them [4], are theoretically able to perform some classification tasks, and some applications for the analysis of foodstuffs have been developed. Two other global analysis methods based on mass spectrometry (MS) were developed with success for classification purposes. The first one analyzes total headspace using a mass spectrometer, without any prior GC separation [5]. This method, often referred to as an "MS-based electronic nose", has found applications for the rapid characterization of food flavour [6] and some of them will be presented and discussed. The second method is pyrolysis mass spectrometry [7], where a small food sample is pyrolyzed at up to 500°C. The resulting volatile fraction, characteristic of the flavour but also of the matrix composition, is analyzed by a mass spectrometer. For all these rapid instrumental methods, a pattern or fingerprint is obtained for each sample, and extensive data treatment, either by conventional multivariate statistics or artificial neural networks, is necessary for classification and quality control purposes [6]. This technique has also been applied for authentication studies.

However, trying to correlate global flavour profiles or quantified flavour components in a food to the sensory perception experienced when eating this food is very often unsuccessful. In other words, it is not enough to know the exact composition of food in terms of flavour compounds to understand perfectly the perception of its flavour, and this remains challenging. Moreover, interactions between taste and aroma and interactions of trigeminal sensations with taste and aroma occur and play an important role in global flavour perception [8]. Perception of flavour is a dynamic process [9]. During food consumption, the concentration of aroma compounds at the olfactory epithelium varies with time as they are released progressively from the food during chewing. Release kinetics depend on the composition of the food matrix and on individual mastication behaviour. Sensory methods, such as time-intensity, have been used to study the time-related aspects of flavour perception [9]. Methods that measure volatiles directly in the mouth or in the nose have been developed in the last years to obtain data that could reflect the pattern of aroma molecules released from food and that are effectively present at the olfactory epithelium during consumption. A clear advance for real time *in vivo* flavour release measurements (nosespace) was obtained using mass spectrometric breath-by-breath analysis with an optimized atmospheric pressure chemical ionization (APCI) source (reviewed by Taylor et al., [10]). A dedicated APCI source was also connected to an ion trap mass spectrometer, gaining the selectivity and structural capability benefits of tandem mass spectrometry (MS/MS) [11].

These real-time in vivo methods have been used extensively to study the impact of the composition and/or texture of a food product on aroma release during chewing [12, 13] and also the influence of oral physiology (respiration, salivation, mastication, etc..) on aroma release [14]. Different studies conducted on dairy products emphasised that the relationship existing between in vivo aroma release and perception was strongly dependent on the type of texture [15], whereas for yogurt, a direct relation exists between release and perception, for hard cheeses cognitive mechanisms would explain the absence of direct relation. However aroma release is also highly influenced by the masticatory behaviour and saliva composition, hence inducing a great importance of interindividual differences. Working with 50 well characterised subjects eating model cheeses, Guichard et al. [16] showed that a higher masticatory activity induced a higher release during the period before swallowing and that a higher amount of saliva incorporated in the bolus induces a higher aroma release after swallowing.

Perceptual interactions of aroma with sapid compounds may also be studied by this method through controlled delivery of both aroma and sapid molecules to panellists [17, 18].

Another powerful chemical ionization method is proton-transfer-reaction mass spectrometry (PTR-MS). Specificity of PTR-MS compared to other chemical ionization approaches is that the generation of the reactant ion and the chemical ionization process are spatially and temporally separated. Individual optimization is therefore possible and quantification is made easier. Since the early works conducted ten years ago on headspace flavour volatiles that used PTR-MS, nosespace applications developed rapidly. A recent development combined PTR and time-of-flight (TOF) mass spectrometry, affording the mass resolution that allows isobaric ions to be discriminated.

The dynamics of aroma release from candies varying in texture modulated by their gelatine content (0, 2, 5 and 15 % w/w respectively) have been recently investigated using PTR-MS [19] and APCI-MS. Two eating protocols (melting and chewing) have been investigated. The highest *in vivo* release for all the three aroma compounds studied (ethyl hexanoate at m/z 145, diacetyl at m/z 87, (Z)-hex-3-en-1-ol at m/z 83, imparting respectively strawberry, butter and green notes) was obtained with the 2 % gelatine sample. Gelatine content had no significant effect on the headspace/product partition and diffusion properties of the aroma compounds. Aroma release was

residence in mouth were completely different between the two eating protocols, affecting swallowing events. When chewing, initial release rates were found higher and times to reach maximum release intensity (t_{max}) were found shorter for all ions. Chewing also increased maximum release intensities (I_{max}) while decreasing signal persistence. Relationships with the dynamics of perception were investigated with the temporal dynamics of sensations (TDS) method [20] conducted in parallel [21] to the instrumental *in vivo* measurements. Relations could be established, essentially between temporal parameters. Thus, for instance, for the 0 % gelatine sample (melting protocol) perception of the strawberry note perfectly coincided with the intense release of ethyl hexanoate after swallowing. For the 2% gelatine sample (melting protocol), a green attribute was noted on a short period just after swallowing, corresponding to the greater release of ion m/z 83 (hex-3-en-1-ol) obtained for this product compared to the other products. Then a strawberry note dominates, in good agreement with the release curves of ethyl hexanoate. Perception became more complex as the gelatine content increased, and occurred increasingly earlier before swallowing, in good agreement with the kinetics of aroma release. Overall, the strawberry note was found dominant, in good agreement with the ethyl hexanoate headspace/product partition properties and its low perception threshold.

Flavour release and flavour perception are dynamic processes and must be studied using dynamic methods. Dynamic techniques have been developed to study the parameters of flavour release from foods. Parallel increased applications of dynamic sensory methods provide a better understanding of food flavour. However, further work is needed to improve our knowledge of various interactions arising at different levels in the process of food consumption: e.g., interactions between food ingredients, and interactions at the perceptual levels such as taste-aroma interactions, or trigeminal interferences, as these play a fundamental role in overall flavour perception.

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Advanced predictive tools based on holistic and targeted approaches for the analytical-sensory correlation of coffee aroma

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Abstract

Robust and reproducible models were developed to predict the sensory profile of espresso coffee from instrumental data using holistic and targeted approaches. The analytical data were obtained either by analyzing headspace constituents by proton transfer reaction mass spectrometry (PTR-MS) or by quantifying selected aroma compounds with GC-MS techniques. In both cases the analytical data were correlated with sensory profiles from a trained panel. In the holistic approach, 16 ion traces in the head-space were monitored by PTR-MS. In the targeted approach, several of the 42 aroma compounds exhibited a good correlation to specific sensory descriptors and may be used as chemical markers. In both approaches, the correlation is based on a knowledge-based standardization and normalization of both datasets that selectively extracts differences in the quality of samples, while reducing the impact of variations on the overall intensity of coffees. Such model is a very useful tool for future development of coffee blends with specific flavour profiles. The results represent a significant progress in correlating sensory with instrumental data exemplified on one of the most complex aromas, i.e. coffee.

Introduction

Flavor scientists have long been exploring what makes coffee smell so good [1-2]. Analytical chemists have discovered a range of impact compounds contributing to coffee flavor, while sensory scientists have developed hedonic methods for accurate coffee flavor profiling [3-6]. Although both approaches look at the same phenomenon, albeit from different perspectives, correlating instrumental data with sensory profiles has proven to be a difficult task. This is due to two fundamental challenges. First, intensity scales in sensory and analytical measurements are of fundamentally different nature. Sensory attributes are evaluated within an arbitrary range (e.g. 0 to 10). In contrast, instrumental measurements result in signals that are not restricted in intensity, thus leading to very different relationships between the intensities of sensory versus analytical signals. Second, sensory scores are not proportional to concentration and each odorant follows a specific non-linear sigmoid dose-response curve. In contrast, instrumental signals are in general linear with concentration. Hence, diluting coffee by a defined factor will result in instrumental intensities reduced by the given factor leaving the signal intensity ratios unaltered. However, diluting coffee makes its sensory profile not just less intense, but may result in a flavor profile of its own.

In this paper, we demonstrate the feasibility of correlating analytical with sensory data by applying holistic or targeted approaches and adequate analytical techniques (PTR-MS, GC-MS), combined with proper data treatment to selectively extract mutually relevant quality information.

Experimental Methods

Holistic approach. Analytical measurements of 16 characteristic ion traces in the headspace were performed by PTR-MS as previously described [7]. A full description of the experimental set-up is given there, including the treatment of the analytical and sensory raw data.

Targeted approach. A total 42 aroma compounds were quantified by GC-MS using the Isotope Labeling Assay (IDA) method. A detailed description of the approach is given in the proceedings of the 23rd ASIC symposium [8].

Sensory evaluation. This was performed by a trained coffee panel as previously described [7-8].

Results and Discussion

Holistic approach. The result is a powerful predictive tool for coffee sensory profiles (Figure 1), applicable to short cups as well as Lungo coffees. The predictive model was validated on a set of 8 additional coffees. Furthermore, the prediction of sensory profiles can be accomplished by on-line PTR-MS within a few minutes.

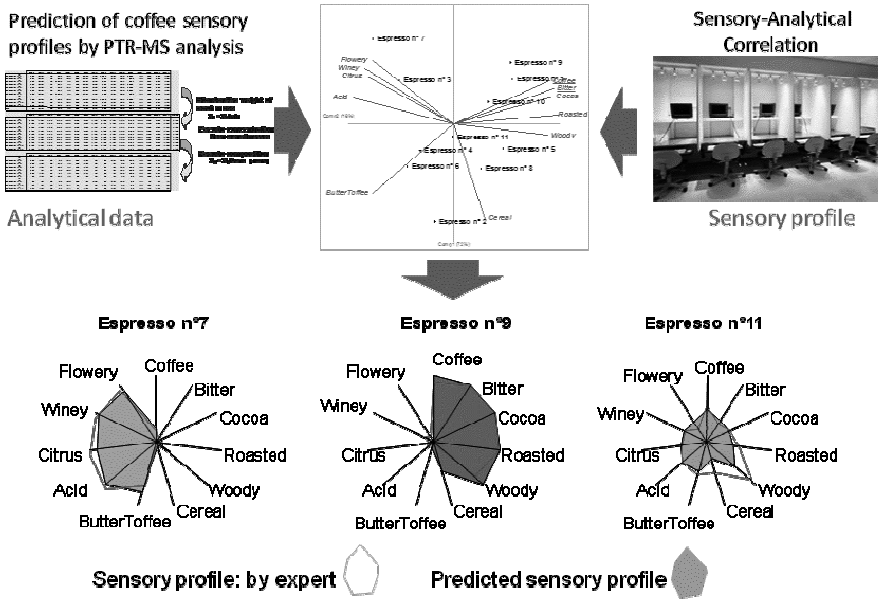

Figure 1: Sensory predictive model. Top line: Selected PTR-MS raw data and sensory profiles are standardized to equal weight. A calibration process allows removing the information of absolute intensities and focusing on data that essentially contain only quality information. Bottom line: Three examples of distinctively different coffees showing the sensory profiles and model results.

These results demonstrate that it is indeed possible to correlate sensory profile of coffee aroma with analytical data, provided that both analytical and sensory datasets are properly standardized and normalized with respect to each other, in order to selectively extract the mutually relevant 'quality' information. In conclusion, the results presented led to a robust model to predict sensory profiles of coffee from analytical data. Furthermore, as the model is based on fast on-line PTR-MS analysis, a prediction of a sensory profile can be accomplished within minutes. Relative to current methods of aroma profile analysis this opens the possibility of high through-put studies.

Targeted approach. The predictive model based on sensory and analytical data produces sensory profiles that are very close to the results obtained by the sensory panel (Figure 2). On a total of 108 predicted attributes (12 coffees with 9 sensory descriptors), only 5 exhibited a deviation from the original value larger than the least significant deviation of the sensory panel. It is important to notice that this model is built on a relatively narrow sensory space (espresso beverages with a volume of 25 mL, 40 mL, and 110 mL), and is valid for this sensory space only. Consequently, it cannot be applied to all coffee products.

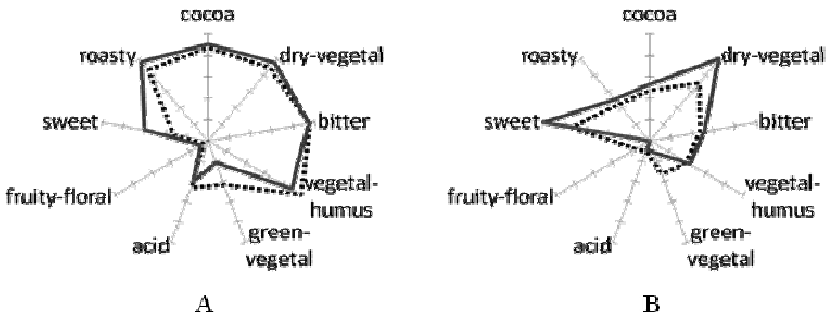

Figure 2: Predictions of sensory data based on a newly developed statistical model as shown for A) Ristretto (25 ml) and B) Lungo (110 ml). Solid lines represent the data obtained from the sensory panel; dotted lines are the predictions of the model.

To establish a model that allows predictions of sensory profiles of espresso coffees based on quantitative analytical data, 12 coffee blends were assessed by instrumental analysis and sensory profiling, and the two resulting datasets were statistically correlated. Several of the aroma compounds analyzed in this study exhibited a good correlation to specific sensory descriptors. The sensory profiles that resulted from the predictive model are in good accordance with the results from the sensory panel. This makes the model a very useful tool to develop coffee blends with specific flavour profile. In conclusion, such predictive sensory-analytical models can be applied to a more molecular-sensory guided development of coffee blends.

The results presented in this paper demonstrate the feasibility of obtaining good correlation between analytical and sensory data. This can be achieved either by a holistic or targeted approach using adequate analytical techniques such as PTR-MS and GC-MS. The critical step, however, is proper data treatment to selectively extract mutually relevant quality information from both (analytical and sensory) data sets.

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Application of PTR MS in food industry for food flavor optimization

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Abstract

Aroma is of a key driver for food quality and consumer preference. Various factors including odorant composition and concentrations as well as the food matrix and oral breakdown determine how we perceive the aroma of a given food. It is therefore of great interest for the food industry to be able to measure, predict and optimize aroma perception. The use of PTR MS contributes to this in monitoring the release of volatiles from foods during consumption. In this paper, the application of PTR MS in food optimization will be illustrated. This includes the application of PTR MS in aroma optimization of low-fat applications, volatile off-flavor masking, encapsulation quality control and satiety studies. Moreover, we demonstrate the versatility of PTR MS e.g. by coupling it to other state-of-the-art food flavor tools (e.g. olfactometer, GC O, gustometer).

PTR-MS: an interesting tool to better understand physicochemical and physiological mechanisms involved in flavour release during food consumption

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Abstract

We proposed a mechanistic and quantitative analysis of aroma release to better describe the influence of physiological, anatomical and physicochemical parameters and interactions that can exist between these factors. This original approach is based on on-line aroma measurements (*in vitro* and *in vivo*) and on *in silico* development and combines several research fields such as sensory analysis, physicochemistry, physiology and modelling. Possible applications include computer-aided product formulation, considering the retronasal aroma intensity as a function of aroma compound properties in food matrices and anatomo-physiological characteristics of the consumers.

Introduction

Consumer choices and preferences are clearly conditioned by food organoleptic properties. The overall perceived flavour of a food depends largely on the way in which stimuli are released in the mouth and transported to receptors during food consumption. Yet, the relationship that exists between stimuli release during eating and perception is quite complex and not well understood because of the existence of perceptual interactions and possibly of other poorly known physicochemical and physiological mechanisms [3].

Stimuli delivery from foods during eating is a complex process, implying physiological, biochemical, physicochemical and physical mechanisms which can interact with each others. To improve product formulation, a better description of these mechanisms is needed. But, because of the complexity and of the inter-individual differences of the consumption processes, few studies developed an integrated modelling approach to describe the amount of released stimuli, taking the whole physiological, physicochemical and kinetic phenomena into account.

Concerning aroma release, the role of food properties (composition and structure) has been largely studied in the literature for different types of real or model foods, notably thanks to the development of rapid and sensitive instrumental technique such as Proton Transfer Reaction Mass Spectrometry (PTR-MS) [1, 2, 10] or Atmospheric Pressure Chemical Ionisation Mass Spectrometry (APCI-MS) [6, 9]. But to our knowledge, the origins and the respective roles of involved mechanisms are still misunderstood.

Recently, a mechanistic mathematical model describing aroma release in the nasal cavity during food consumption of semi-liquid products was built, considering retronasal aroma intensity as a function of transfer and volatility properties of aroma compounds in food matrices and physiological characteristics of consumers [14]. It intends to be a first step towards quantitative mechanistic description of the retronasal olfactory stimulus generation.

Studies conducted in our research group aim at identifying and quantifying the main mechanisms responsible for in-mouth stimuli release. For this purpose, an original multidisciplinary approach combining experimental and modelling aspects is developed. Different types of food in terms of nature, composition and texture as well as different stimuli (volatile and sapid compounds) were used to study specific mechanisms. The implementation of the existing model on the basis of experimental results will help to identify the main mechanisms responsible for in-mouth aroma and sapid release and to better understand how the characteristics of products (composition, structure) and/or individuals (physiological parameters, individual experience) could explain sensory differences.

Approach

Figure 1 schematized the integrated approach we use in the case of aroma release and perception.

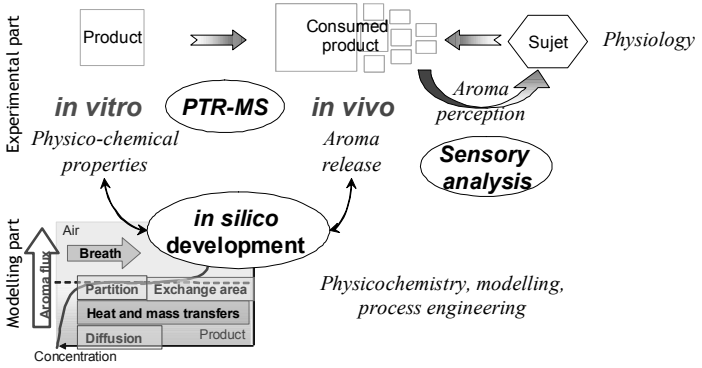

Figure 1: schema of the integrated approach used to better understand mechanisms involved in aroma release and perception during food consumption

The experimental part is devoted to:

- the characterization of food product (*in vitro* measurements). This part includes rheological, physical and physicochemical measurements to describe the main properties of products in terms of structure, texture and composition. In this section, PTR-MS equipment is notably used to determine some key physicochemical properties of aroma compounds (air/product partition and diffusion properties) from *in vitro* measurements of aroma release [8];
- the characterization of *in vivo* aroma release during food consumption (*in vivo* measurements using PTR-MS) by subjects ;
- the characterization of perceptions using sensory analysis. Sensory profiling is classically used to obtain the overall sensory picture of products. In addition, the use of dynamic methods such as the TDS method (Temporal Dominance of Sensations, [7]) enables to evaluate the temporal dimension of perceptions. This dynamic characterization is quite interesting as it can be related to aroma release data to go further in the understanding of involved mechanisms;
- physiological measurements, performed to take subject characteristics into account.

In parallel, a mechanistic modelling approach, based on mass transfer analysis within each compartment of the system, is used to describe *in vitro* and *in vivo* release. The comparison of model predictions to experimental data enables to determine some key physicochemical properties and to identify the main mechanisms that can explain release data:

- concerning *in vitro* release, the adjustment of a mechanical model to experimental kinetics led to the determination of both air/product partition and diffusion properties of aroma compounds (VASK method [8]);
- concerning *in vivo* release, the model, based on the physiology of the swallowing process, provides reasonably accurate time predictions of the relative aroma amount in the nasal cavity and is able to simulate successive swallowing events as well as imperfect velopharyngeal closure.

Results

This integrated approach was applied on several types of foods (liquid to gelled products) to better understand the role of product composition and/or structure and of subject on aroma release.

Concerning the study of flavoured carbonated beverages, the effect of two composition factors (sugar and CO_2) was investigated on both the sensory and physicochemical properties of drinks by studying *in vitro* and *in vivo* aroma release. Sensory results revealed that the presence of CO_2 increased aroma perception regardless of the sugar content. In agreement with volatility parameters, *in vivo* measurements showed that carbonated drinks released a greater quantity of aroma compounds in the nose space than non-carbonated ones. CO_2 seemed thus to induce large modifications of the physicochemical mechanisms responsible for the aroma release and flavour perception of soft drinks. Moreover, sugar content seemed to have an impact (increase) on aroma perception only in the case of non-carbonated beverages. Sensory interactions were thus observed, in particular, between sweet and aroma perceptions. For carbonated beverages, sugar content had an impact only on aroma release, but not on their perception [11, 12, 13].

The role of candy texture (induced by a variation of gelatine content) on the dynamics of aroma release was studied by applying simultaneously dynamic instrumental and sensory methods [4,] Saint Eve*, et al.*, 2010). The highest *in vivo* release was obtained for the 2%-gelatine sample for all aroma compounds. The dominant sensation for the liquid product was the “strawberry” note. For other products, the temporal characteristics of perceptions were more complex. The global duration of the dominance period (all sensory attributes taken together) increased linearly with gelatine content. Data highlighted that aroma release resulted from interaction between product properties and oral behaviour. Some relations with the dynamics of perception have been established, essentially between temporal parameters.

A similar approach was applied to evaluate the impact of swallowing on aroma release and perception in the case of the consumption of alcoholic beverages. The comparison of results obtained with two protocols (spitting out or swallowing of the product) highlighted significant differences in both the perception and the release of aroma: the swallowing of the product resulted in more complex perceptions, but decreased the dominance rates of aromatic attributes. Ethanol perception also had an impact when the product was swallowed. Aroma release data partly accounted for the differences in perception, particularly as concerned ethanol release. Some relationships between sensory and physicochemical data have been established, particularly as concerns the temporal dimension of sensory and release phenomena [5].

Concerning product effect, the role of food bolus viscosity on aroma compound release, independently of others physico-chemical phenomena (such as mass transfer or partition coefficients) was also considered. A sensitivity analysis of the model enabled us to determine that mass transfer and partition coefficients (the products properties), as well as air flow rates and volumes of upper airway (physiological parameters) had the highest influence on release kinetics. The thickness of the residual product layer coating the pharyngeal mucosa -resulting of the

interaction subject / product- has also a strong influence on the aroma release kinetics but is difficult to measure experimentally. Different hypothesis on mechanisms responsible for product coating the pharyngeal mucosa were investigated by confronting the *in-vivo* aroma release data with the model predictions.

Conclusion

Combining PTR-MS measurements, sensory analysis and modelling investigation allowed us to identify the respective role of product properties and subject behavior on aroma release. It permits to go further in understanding the relationship between release and perception in order to optimize flavored food formulation.

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Process Monitoring by PTR-ToF-MS : Applications on Profile Roasting of Coffee

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Abstract

The time-temperature roasting profile is thought to have a major influence on the flavor of the roasted coffee [1-3]. Coffees were roasted to a fixed roast degree along different time-temperature profile. On-line analysis by PTR-ToF-MS gave insight into the real-time dynamic release of volatile flavor compounds (VOCs). The on-line data were complemented by off-line analyses of the coffee brew. This included Headspace Solid Phase Micro Extraction Gas Chromatography Mass Spectrometry (HS-SPME-GC-MS) and sensory evaluation. Combining the information from all three datasets, a concerted interpretation of the impact of the roasting profile on the flavor of the brew is attempted.

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Applications of Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-TOF-MS) to Monitor *In-vitro* and *In-vivo* Flavour Release from Model and Real Systems

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Abstract

Applications of PTR-MS in monitoring in-vivo aroma release have been described as the ideal technique in relation to its sensitivity, dynamic on line capability and rapid response time. However, there exits some limitations for conventional quadrupole PTR-MS currently used for in-vivo analysis. In principle, quadrupole mass spectrometers are limited to analysing only one channel at a time. Thus resulting in the switching of the detector between the *m/z* (mass to charge ratios) when simultaneously analysing more than one mass. In this mode, there exists a compromise between the number of *m/z* monitored and the signal to noise ratio [1]. Moreover, the analysis of complex food systems using quadrupole PTR-MS often results in difficulties in unequivocal compound identification and, more critical in nose space analysis, superposition of signals originating from different compounds. PTR-TOF-MS technique has proven capabilities in mass accuracy providing unambiguous determination of chemical formula leading an improved interpretation of mass spectra [2], whilst providing complete spectra in a split second.

In this study, beside using it for rapid head space characterization *in vitro*, we demonstrate that PTR-TOF-MS provides improved selectivity and resolution of some masses that enables a step forward, in measuring aroma delivery to human assessors during nose space analysis, allowing a better understanding of the contribution of product composition in a complex food system to aroma release during consumption. With this contribution we demonstrate, to the best of our knowledge, for the first time the use of proton transfer reaction time of flight mass spectrometry (PTR-TOF-MS) in the measurement of flavour release from food during consumption. We investigated both a model and a real system.

In the first case study PTR-TOF-MS was applied to better understand the influence of sugar content on flavour release in a baked model cereal bar system. A synthetic strawberry flavour comprised of 17 different known flavour active compounds was used in the preparation of baked cereal bars. Distinguishable differences were shown for the release of volatile compounds between samples with different levels of sugar and polydextrose concentrations during both in vitro and in vivo measurements. Improved mass resolution and speed of PTR-TOF-MS enabled direct comparisons between the rate compounds reached the nose space, maximum nose space concentration of compounds, and the time after which compounds are no longer detected in the nose-space. The measurement of all relevant peaks at a time is possible without any preliminary mass selection allowing for reduced experimental time, improving data consistency and lessening participant fatigue. These findings present a new and powerful interpretation of flavour release in baked cereal matrices and demonstrate promising opportunities for the use of PTR-TOF-MS in

flavour release studies. In particular we indicate that relative compound abundance in nose-space data can be different from those obtained by head space measurement and that product formulation will influence the release of volatile compounds differently depending on the properties of the volatile compound itself (Figure 1).

In the second case study we investigate whether it is possible to detect differences induced by ageing wine in barrels of different brands. The same wine made from red grape Lagrein, harvested on 15/9/2009 in the same vineyard, was aged after fermentation in barrels of 5 different brands and in a stainless steel vat as a control. The aim is to follow the effect of ageing the wine in contact with different types of wood in comparison to the aging in stainless steel.

Headspace analysis of diluted wine samples showed discrimination of wine aged in wood barrels from wine aged in stainless steel and, more interestingly, partly distinguished among wines aged in different barrels alone. Nose space analysis of wine sample is more difficult because of assessor variability, which cannot be completely removed. It is however possible to confirm, some differences among wines aged in different barrels from nose space measurements in conjunction with headspace results.

In conclusion we provide examples of the application of PTR-TOF-MS both for the rapid characterization of samples and for the monitoring of the release of flavour during food consumption. In particular we evaluate i) a model system (flavoured cereal bars) identifying interesting effects of sugar content both on the intensity and release time of the known flavour compounds and ii) a real system, wine aged in barrels of different brands, rapidly identifying differences in the head space composition and demonstrating also an effect on the actual nose space concentration during wine consumption.

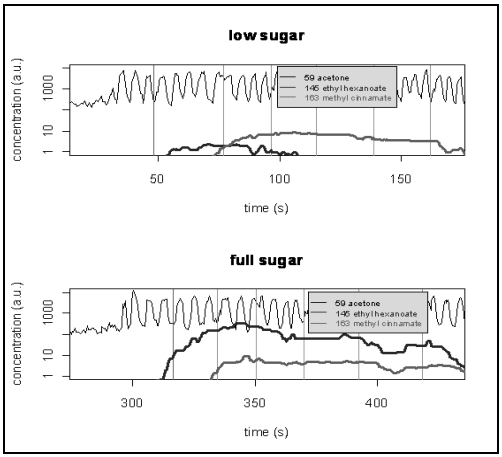

Figure 1: Example of nose space measurement of flavoured cereal bars with different sugar reduction. The red vertical line indicates the time when samples were placed in the mouth, while green lines show times of swallowing. The effect of sugar reduction is very different for ethyl caproate and methyl cinnamate both on the concentration and on the time evolution.

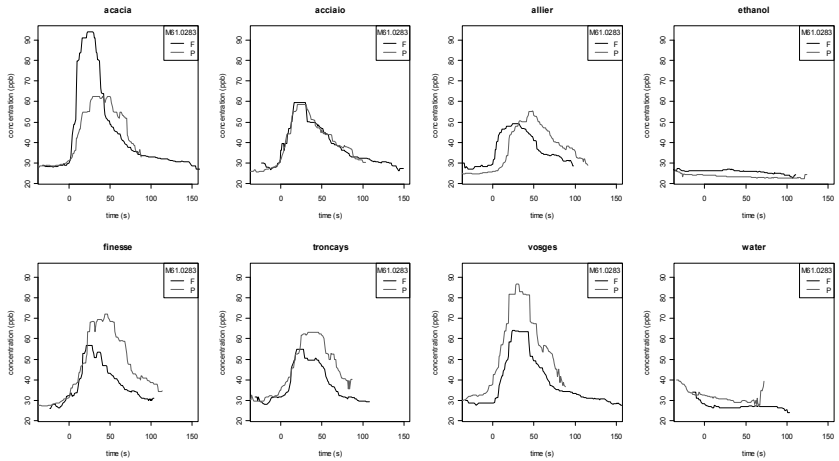

Figure 2: Example of nose space measurement of wines aged in different barrels. The two lines represent two different assessors; the different panels correspond to different wines. Data obtained with ethanol/water solution and with pure water are shown on the right panels as references. Running median on 25 points is used to remove the effect of the breathing tidal response.

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PTR-MS continuous measurement of VOC emitted from freshly cut onion

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Abstract

Volatile organic compounds (VOC) were continuously measured by PTR-MS during the first 120 min after cutting of onion (*Allium cepa* L). The headspace composition changed rapidly due to the very reactive volatile sulphurous compounds emitted from onion tissue after cell disruption. From 0-15 min, m/z 91 dominates and hereafter m/z 41, 43 and 151 dominated. M/z 91 was assigned to the lacrymatory factor; propanethiol S-oxide. M/z 151 was assigned as dipropyl sulphide and m/z 41 and 43 were assigned as fragments of mainly propanethiol and dipropyl disulphide. These were the main compounds emitted during 30-120 min after cutting. Monitoring the rapid change of VOC's in the headspace of cut onion necessitates high time resolution. By PTR-MS the headspace of cut onion can be measured directly after cutting without extraction or concentration. The advantage of high time resolution, low detection limits and ease of application with no need for extraction and concentration makes PTR-MS an obvious choice for measuring VOSC emitted from cut vegetables. Application of PTR-MS is demonstrated to provide new information on temporal variation in chemical composition of cut onion headspace following cutting.

Introduction

Freshly cut onion (*Allium cepa* L.*)* immediately brings tears into our eyes and soon after cutting a distinct onion odour develops in the kitchen. The tears and the odour are caused by very volatile and reactive sulphurous compounds. Cellular disruption of onions and other *Allium* vegetables leads to a mixing of cellular contents and induction of numerous chemical and enzymatic reactions not normally present in the intact tissue. Reactions associated with the *S*-alk(en)yl cysteine-sulfoxide pathway result in an immediate synthesis of numerous sulphur volatiles with a potential to contribute to the aroma and flavour of *Allium* vegetables. The emitted volatiles are very volatile and reactive and therefore difficult to measure. These obstacles are reflected in the current research, which show different results in determining the specific compounds emitted after cutting. Järvenpää et al. (1998) use solid-phase microextraction (SPME) for gas chromatography (GC) analysis and find the lacrymatory factor 1 min after cutting and dipropyl disulphide 30 and 170 min after cutting and no thiosulphinates [1]. Arnault et al. (2000) also use SPME for measuring the lacrymatory factor and disulphides [2]. They claim that the disulphides are degradation products of thiosulphinates and measure the thiosulphinates by direct injection of diethyl ether extracts into the GC, and in these measurements no disulphides occur [2]. Both methods imply that the time between each sample point does not correspond with the dynamics of emitted volatiles. Recently Kubec et al. (2010) used direct analysis in real time-mass spectrometry (DART-MS) for monitoring *Allium* chemistry [3]. In the method a capillary is used to puncture the plant material and the capillary is positioned in the sampling position. The method is continuous, but the lowest mass is m/z 55 and the amount of plant material actually analysed is very little compared to the size of an onion bulb.

The advantage of high time resolution, low detection limit and ease of application makes PTR-MS an interesting choice for measuring VOC's that are emitted from disrupted *Allium* tissue. The present study investigated the use of PTR-MS to identify the potent aroma volatiles emitted from onions during the first 120 minutes after cutting.

Experimental Methods

An onion bulb was peeled and cut in approximately 0.5×0.5 cm pieces and 50 g was rapidly transferred to a 1 L blue cap flask and the measurement started immediately. Filtered (Supelco, Supelpure HC 2-2445-U, Bellefonte, PA, USA) air was used as inlet gas and was led by Teflon tubes through holes in the top of the cap. The outlet of the flask was connected directly to the PTR-MS. The flow was driven by the inlet into the PTR-MS and set to 100 ml/min. Measurements were done at room temperature during the first 120 min after cutting.

For identification of the formed VOC's, reference mass spectra were obtained by adding a few drops to a 2 ml glass vial covered by a polypropylene cap with PTFE/silicone septa. A small hole was introduced into the septum with a needle. This vial was placed in a 100 ml blue cap flask with inlet and outlet tubings for PTR-MS measurements.

For measurement of VOC's from freshly cut onions and reference mass spectra, a commercial PTR-MS apparatus was used (IONICON Analytic Gmbh, Innsbruck, Austria). The drift tube conditions were: 2.15 mbar, 60°C, and 600 V, corresponding to an E/N of 138 Td. The mass spectrometric data were collected over a mass range of m/z 21-200 using a dwell time of 0.2 s. The PTR-MS was setup for continuous acquisition of mass scans, and the measurement interval was 18 seconds. All connections were made with Teflon tubes. The inlet flow rate was set to 100 ml/min.

Results and discussion

Immediately after cutting m/z 91 appeared and reached maximum after 1 min. This mass decreased and practically disappeared 20 min after disruption of the cells. The m/z 91 can be assigned as the molecular protonated ion of propanethial S-oxide; the lacrymatory factor in onions. The finding of the compound and the timeframe correspond well with other records [1, 2].

M/z 59 appeared during the first 10 min, stayed at a high level for app. 50 min and then disappeared slowly during the next 60 min. The m/z 59 was assigned to acetone. A record of PTR-MS measurements of crushed garlic also finds acetone [3].

After 15 min, m/z 41, 43, 77 and 151 appeared and the masses continued to rise until 60 min, where they started to decrease. Despite this decrease, m/z 41, 43 and 151 continue to dominate until the end of the measurement after 120 min. The m/z 77 and 151 can be assigned to propanethiol and dipropyldisulphide. Due to light fragmentation of dipropyl disulphide in the drift tube, the compound gives rise to m/z 41 and 43, but propanethiol also fragments significantly into m/z 41 and 43 with the parent protonated ion m/z 77 also being present. By the use of the relation between m/z 151, 77, 43 and 41 in the reference mass spectra it could be concluded that the main compounds emitted 30 to 120 min after cutting was propanethiol and dipropyl disulphide. Only very small amounts of thiosulphinates were detected.

The finding that propanethiol is a major part of the headspace of cut onion, has not been reported before. It is proposed that the differences between these results and various records mostly can be traced back to the sampling procedure and the processes needed to bring the VOC's from the headspace of the plant material to the measuring unit [1, 2, 3]. The sampling procedure used in

this study is very simple and the possibility of inducing errors therefore less. The composition of the headspace of freshly cut onion changed rapidly and this indicate the need for measurements with high time resolution. The results show that PTR-MS can be used to give new information about the compounds emitted from cut onion with high time resolution.

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Influence of polyols and bulking agents on flavor release

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Abstract

PTR-MS was used to characterize the release of three aroma compounds from aqueous solutions containing mixtures of the polyol erythritol and the bulking agents polydextrose and oligofructose. The most volatile compounds benzaldehyde and ethyl butyrate were retained more readily in low-viscosity solutions in the presence of the polyol and bulking agents compared to in pure water. In contrast, an increased release of the less volatile *cis*-3-hexen-1-ol was observed. High-viscosity solutions were also investigated and a clear correlation was found between the viscosity of the solutions and aroma release. The release of all investigated aroma compounds decreased with increasing solution viscosity. Because this correlation was not evident in the low-viscosity solutions, it is assumed that aroma release is only significantly influenced by the substrates when a critical concentration (c*) is exceeded.

Introduction

Obesity is currently a major health issue, with excessive sugar intake playing a significant role in its occurrence. Thus, it is of great importance to find alternatives to the common sugars. Conventional food products must be modified to sugar-reduced or sugar-free formulations, which not only influences the food texture, but also the release of aroma compounds. A clearer understanding of physico-chemical interactions between volatile flavor molecules and the non-volatile sugar-free constituents of a food matrix would therefore help to adapt the texture and release of flavor compounds to those of conventional sugar containing food products.

Interactions between water (the predominant constituent of many foods), non-volatile food ingredients, and flavor molecules have been widely studied and are characterized by hydrophobicity (log P value) and volatility (gas-liquid partitioning coefficient, k_H) of the latter [1,2]. The texture of aqueous solutions and gels is also known to directly affect the release of flavor compounds. As the viscosity of a solution increases, a decrease in aroma intensity and therefore flavor release is generally observed [3].

In this study, specific polyol and bulking agent solutions were investigated to characterize their influence on flavor release. PTR-MS was employed to study the mechanisms of aroma release from low-viscosity and high-viscosity solutions. Furthermore, the influence of the rheological behavior of the solutions on aroma release was studied.

Experimental Methods

Individual aqueous solutions of erythritol, polydextrose and oligofructose were prepared at concentrations of 0% and 20% (w/w), respectively. Mixtures of the solids were investigated at concentrations of 43% (w/w). The substances were dissolved in tap water and concentrated under

heat to the required dry matter content. The flavor compounds were mixed thoroughly with 25 mL of the solutions, which were then equilibrated at room temperature for 15 min.

Different initial concentrations of each aroma compound were chosen to provide optimum mass spectrometric detection and were as follows: 2.2 mg L^{-1} ethyl butyrate, and 4.5 mg L^{-1} *cis*-3-hexen-1-ol and benzaldehyde. Thus, the orthonasal intensity of the aroma compounds in the solutions was clearly perceivable without being obtrusive. An experimental D-optimal mixture design using Design Expert (v. 6.0.10, Stat Ease Inc., Minneapolis, USA) was chosen to compose the mixtures with a dry matter content of 43% [4].

Headspace analysis by PTR-MS

Headspace analyses were conducted using a high sensitivity PTR-MS (hs-PTR-MS, Ionimed Analytik, Innsbruck, Austria). 25 mL portions of equilibrated solutions were analyzed. The sample was continuously stirred and maintained at a temperature of 37±1°C to simulate body temperature conditions. The headspace above each solution was flushed with 1000 sccm zero-air, 370 sccm of which was drawn into the inlet of the PTR-MS instrument. The PTR-MS inlet and reaction chamber were maintained at 60°C. A constant drift voltage of 400 V was employed and each flavor compound was measured with a dwell time of 10 s. Initial mass spectral analysis of each of the investigated flavor compounds revealed the predominant product ion mass-to-charge ratio (m/z) (Table 1), which were chosen for subsequent analyses in selected ion mode. The PTR-MS instrument was calibrated for the three flavor compounds using a prototype liquid calibration unit (LCU, Ionimed Analytik) to determine the sensitivity, ε.

Compound	Formula	Molecular weight [g mol^{-1}]	Log P value	Henry's law constant k_H [m atm^{-1}]	Sensitivity ε [ncps ppb_V^{-1}]	Predominant *m/z*
cis-3-Hexen-1-ol	$C_6H_{12}O$	100	1.61	64.5	13.2	83
Benzaldehyde	C_7H_6O	106	1.64	37.5	14.0	107
Ethyl butyrate	$C_6H_{12}O_2$	116	1.77	2.5	8.1	117

Table 1: Aroma compounds investigated by PTR-MS.

Data analysis

The transmission-corrected and normalized signal intensities of the product ions were converted to volume mixing ratios (VMR) according to the sensitivities given in Table 1. In order to provide specific quantities with which to characterize and compare aroma compound release curves, the following parameters were calculated for each compound and sample matrix: maximum VMR of the release profile (I_{max}), time to reach I_{max} (t_{max}), and gradient of the release curve ($\Delta y/\Delta x$).

Apparent viscosity, η [Pa·s], was chosen to characterize the texture of the aqueous solutions and was measured with a Bohlin CVO 100 shear rheometer (Malvern Instruments Ltd., Worcestershire, UK) at 37°C using a constant shear rate of 11.5 s^{-1}.

Results and Discussion

The aim of this study was to characterize the aroma release from low and high-viscosity aqueous solutions of erythritol, polydextrose and oligofructose at their thermodynamic equilibrium using dynamic headspace PTR-MS measurements. Of the three investigated flavor compounds, *cis*-3-hexen-1-ol showed the highest t_{max} value and the most moderate $\Delta y/\Delta x$ gradient from pure water and the low-viscosity solutions, offering a relatively slow release of this compound (Figure 1).

This may be explained by strong hydrogen-bond interactions with water molecules in the sample matrix. *cis*-3-Hexen-1-ol was the most hydrophilic and furthermore the least volatile of the flavor compounds investigated (Table 1). Hence, hydrogen bonds with water molecules must first be broken in order to allow the release of the molecules into the gas phase. Benzaldehyde and ethyl butyrate showed smaller interactions with the polar water molecules, resulting in low t_{max} values and higher initial release rates than *cis*-3-hexen-1-ol (Figure 1). In general, the more hydrophobic and volatile the flavor compounds, the more rapidly they are released from water and the low-viscosity solutions [1,2], which is consistent with our observations.

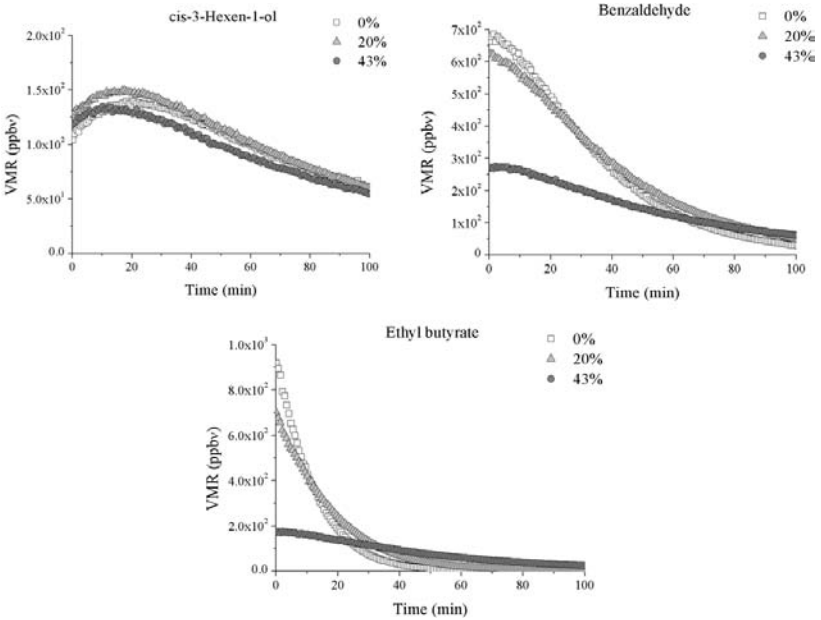

Figure 1: Aroma release of cis-3-hexen-1-ol, benzaldehyde and ethyl butyrate from □ aqueous solution 0% (tap water), Δ aqueous solution 20% (20% erythritol), and ○ aqueous solution 43% (14.3% erythritol, 14.3% polydextrose, 14.3% oligofructose).

The relative release of each flavor compound from the low-viscosity solutions, expressed as a fraction of the maximum headspace concentration in pure water, was also investigated. *cis*-3-Hexen-1-ol was released more extensively from the polyol and bulking agent solutions at concentrations of 20% (w/w) than from water. In contrast, the other volatiles showed an increased retention in the presence of the solids at concentrations of 20% (w/w) (Figure 1). An inconsistent flavor release from carbohydrate matrices has been reported in the literature [2,5,6]. Polyols and bulking agents are able to absorb water molecules. Due to the hydration of these molecules, a general loss of unbound water in the solution seemed to occur, whereby most likely less water molecules are subsequently available as a solvent for *cis*-3-hexen-1-ol molecules, leading to a higher volatility of this flavor compound [7].

Figure 1 also depicts the release of the flavor compounds from high-viscosity solutions. It is evident that benzaldehyde and ethyl butyrate were retained most in high-viscosity solutions. *cis*-3-Hexen-1-ol demonstrated a similar behavior, albeit with much lower variation in the release between the solutions with varying viscosities compared to benzaldehyde and ethyl butyrate. This observation may be due to the phenomenon described above: *cis*-3-Hexen-1-ol was released more

readily from low-viscosity solutions than from water due to a general loss in unbound water. This effect seems to be compensated by increasing dry matter content. Statistical analysis of the experimental mixture design offered a correlation between the rheological behavior of these solutions and flavor release. A detailed study of the investigated mixture design is reported in the literature [4]. This correlation was not evident in the investigated low-viscosity solutions and it is assumed that the aroma release is only significantly influenced by the substrates when a critical concentration (c*) is exceeded, as has been previously reported in the literature for polymers [8].

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Measuring aroma release from hot water based food applications by PTR-MS

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Abstract

PTR-MS measurements of aroma release can be performed on very different products (e.g. palm wine [1], yogurt [2], whey protein gels [3], etc.). Taking aroma release from instant soups during preparation as an example, it will be discussed which properties of the chosen aroma compounds, delivery systems, food application, and experimental set-up have to be taken into consideration and how the obtained results (e.g. the time to reach maximum release) can be correlated to these properties.

Introduction

Characterising aroma release from food is done by measuring the release curve over time and by quantifying the total amount of released aroma. These parameters depend on several conditions:

- Aroma compounds can be released during food preparation (in vitro) or during food consumption (in vivo).
- Temperature, agitation rate, air flow above the product, etc. produce different release situations.
- Physico-chemical parameters of each aroma molecule (like volatility or solubility) vary within a huge range, resulting in specific interaction with food matrix of a given composition.
- Last but not least the micro-environment of aroma compounds can be influenced by different types of delivery systems, thus influencing the release behaviour.

For the interpretation of aroma release measurements it is important to take into consideration that measured indicators are not only influenced by one but by all of the mentioned conditions.

Results

Aroma Compound Selection

To obtain as much information as possible aroma chemicals have to be selected within a wide range of molecular properties. A plot of compound hydrophobicities (expressed as partition coefficient oil –water) and compound volatilities (expressed as partition coefficients air-water) is useful for this selection (Figure 1).

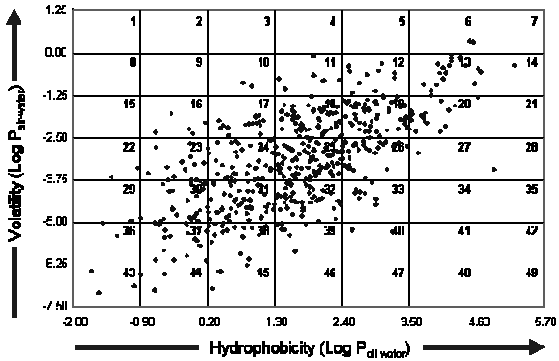

Figure 1: Aroma compound volatilities in water plotted against their hydrophobicities.

Adding a grid pattern on this plot facilitates the selection of compounds from each hydrophobicity-volatility cluster. Limitations are:

- too low volatilities, i.e. the amount of compound in air will be too low to be detected;
- too high hydrophobicities, i.e. it will not be possible to solubilise a sufficient amount of this compound in water.

Other criteria for compound selection are fragmentation patterns, overlapping signals from other aroma compounds, the ratio of odor activity vs. instrument sensitivity, and background signals from food application.

After selecting the aroma compounds their optimum concentrations have to be determined. The concentration must be high enough to release sufficient aroma amount into the headspace for PTR-MS detection at the given conditions and low enough to be below the solubility level. At the same time the measured PTR-MS signal has to be within the linear range of the instrument.

Experimental Conditions

The experimental set-up influences the results. Figure 2 compares two measurements of methyl salicylate release from hot water which were performed under different conditions:

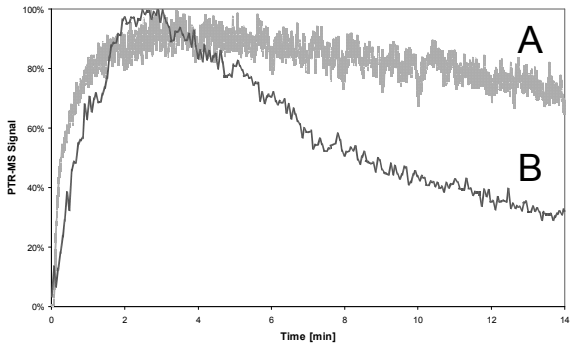

Figure 2: Methyl salicylate release from soluble matrix when hot water is added. A: closed system with controlled air flow, headspace exchange every 2 min, constant temperature (85°C). B: open system, temperature decreases from 85°C to 50°C during the measurement.

Aside from temperature and air flow other parameters that influence aroma release are:

- Dimensions of the vessel
- Stirring rate
- Possible aroma adsorption within the system.

Determination of T_{max}

In general the goal of aroma release experiments is to investigate the interactions of aroma compounds, food matrices and delivery systems. To this end it is necessary to determine indicators which can be used for comparison of different aroma compounds, different food matrices or different delivery systems. Indicators which are mostly used [3, 4] are:

- Maximum intensity (I_{max})
- Area under the curve (AUC)
- The time which is needed to reach maximum intensity (T_{max})

Figure 3 demonstrates the effect of molecular properties and delivery system on the release of 4 compounds when hot water is poured on instant soup powder (data taken from manuscript "Characterization of release kinetics of aroma compounds from encapsulation systems in hot water applications", by Segolene Leclercq and Robert Wieland submitted to Journal of Microencapsulation, 2010).

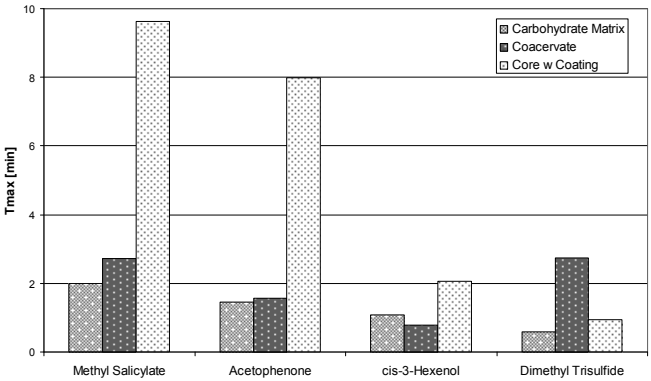

Figure 3: Time to reach maximum release (Tmax) for selected compounds in different Delivery Systems when hot water (85°C) is added.

To extrapolate findings of release experiments to other aroma compounds it can be tried to link measured indicators with compound's property parameters. In the case of the hot soup for example it was found that:

- for aroma compounds which are encapsulated in a fast dissolving carbohydrate matrix, the time to reach maximum release is decreasing with increasing compound volatility (i.e. increasing partition coefficient air-product, Figure 4);
- the same relation is true for compounds released from a coated carbohydrate core – but with much longer T_{max} if the compound volatility is relatively low (Figure 4);
- for aroma compounds which are released from an oil droplet in a coacervate delivery system the time to reach maximum release is decreasing with increasing hydrophilicity (i.e. increasing partition coefficient water-oil, Figure 5);

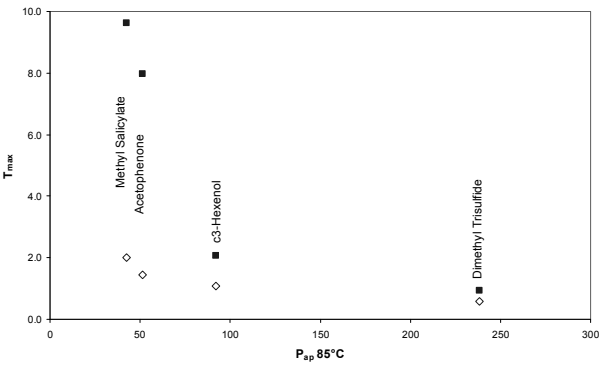

Figure 4: Correlation between compound volatilities from soup (expressed as partition coefficient air-product, P_{ap} at 85°C) and measured time to reach maximum release (T_{max}) from carbohydrate matrix (◊) and coated carbohydrate core (■).

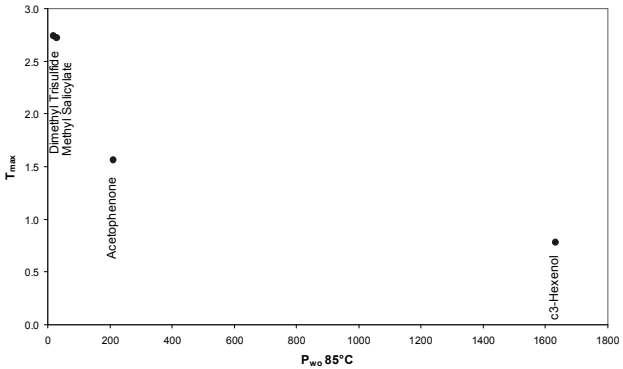

Figure 5: Correlation between compound hydrophilicities (expressed as partition coefficient water-oil, P_{wo} at 85°C) and measured time to reach maximum release (T_{max}) from coacervate (●).

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Monitoring endogenous flavor compounds formation in fermented milks by PTR-ToF-MS: modeling of fermentation processes and study of matrix impact

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Abstract

In the present study PTR-ToF-MS has been used as an alternative and effective technique for the monitoring of different processes relevant for quality control and good manufacturing practices (GMPs) in the dairy industry. Different applications of PTR-ToF-MS related to the rapid and non-invasive monitoring of VOCs are herein demonstrated including: a) the detection of several VOCs of relevance for the dairy industry, b) the rapid monitoring and modeling of VOCs evolution during lactic acid fermentation, c) the study of the impact of milk base supplementation and matrix formation (liquid to sol-gel transitions) on the endogenous VOCs release in real and model acidified dairy systems.

Introduction

The market of fermented milks is one of the most profitable sectors of the dairy industry owing its constant expansion over the last years to the awareness of consumers for healthy, nutritive and savory foods. The flavor of fermented milks is very peculiar as apart from the added flavoring agents, a number of endogenous VOCs are present and contribute to the formation of a characteristic sour-buttery-refreshing flavor. The development of an equilibrated flavor depends on proper manufacturing processes such as: the selection of raw materials, the pasteurization-homogenization steps, the incubation-fermentation conditions and the packaging-storage handling (Tamime & Robinson 2007); the fermentation process being the most important as it is primarily related with the formation of the endogenous VOCs. Aim of this study, was to evaluate the potential of PTR-ToF-MS as a technique for the measurement of VOCs found in dairy products for quality control purposes.

Experimental Methods

Monitoring of the volatile compounds during the lactic acid fermentation

Fermented milk samples were prepared by non-fat (0.3% milk-fat, 8.4% SNF), low-fat (1.5% milk-fat 8.4% SNF) or full-fat (3.5% milk-fat, 8.3% SNF) ultra-high pasteurized milk (Mila Spa., Bolzano, Italy), The stock starter culture was prepared by dissolving a freeze dried yogurt culture containing Streptococcus thermophilus and Lactobacillus delbrueckii subsp. bulgaricus (Sacco Srl., Italy) in MilliQ water to a concentration of 1U/mL (Soukoulis et al., 2010). Samples of fermented milks were withdrawn during the incubation, rapidly cooled at 4°C and stored at the same temperature for 2h before headspace analysis to avoid over-acidification.

Effect of milk base supplementation on the endogenous VOCs concentration in yogurt headspace

Fourty yogurt systems (set and stirred style) differing on their milkfat content (0.3% and 3.5% w/w), protein fortification level (0% or skim milk powder added in the level of 3.5% w/w) and added modified tapioca starch concentration (0, 0.5, 1, 1.5 or 2.0% w/w, Farinex VT 60, Avebe, Veendam, The Netherlands) were prepared according to the previous procedure, and stored at 4°C for 48h prior analysis in order to achieve gel stabilization.

Matrix impact on the evolution of endogenous flavor compounds during the fermentation process

Simplified real and model systems based on reconstituted milk (0.3% milkfat and 8.4% SNF) were prepared, the latter including standard flavor compounds as acetaldehyde (Fluka), 2-propanone (VWR), diacetyl (Sigma-Aldrich), acetoin (Sigma-Aldrich), 2.3-pentanedione (Fluka), and 2-heptanone (Sigma-Aldrich), at a fixed concentration (1ppm) in the reconstituted milks. Acidification of model systems was carried out by adding 2% w/w Glucono- δ-lactone (GDL) and consequently incubating them at 42°C until reaching the pH end point (pH=4.5).

PTR-ToF-MS measurements of samples headspace

Cooled acidified milk samples were placed in 1L glass jars supplied with Teflon/silicon septa on opposite sides and incubated (28 ºC, 30 min) before headspace measurements. Measurements were carried out by a commercial PTR-ToF-MS 8000 instrument from Ionicon Analytik GmbH (Innsbruck, Austria) in its standard configuration (V mode). Sample preparation and analysis were performed following the procedure described in (Soukoulis et al., 2010). The sampling time per channel of ToF acquisition is 0.1ns, amounting to 350000 channels for a mass spectrum range from m/z 10-400, and the ionization conditions in the reaction chamber were maintained at 600 V for drift voltage and 2.25mbar for drift pressure. Thus, the instrument was operated at an E/N value of 140 Td. Internal calibration and peak extraction was performed according to the procedure described Cappellin et al. (2010).

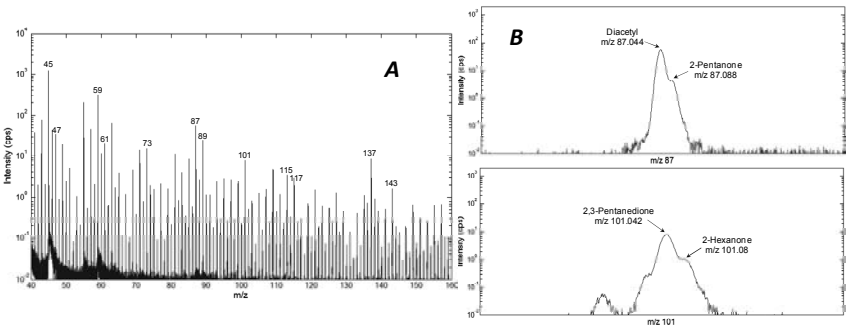

Figure 1: A: Low mass region representation of the average spectrum of unfortified full fat yogurt samples with different amounts of tapioca starch acquired by PTR-ToF-MS. B: Two mass spectral regions (at m/z 87 and 101) corresponding to four important flavor compounds present in dairy products (diacetyl, 2-pentanone, 2,3-pentanedione, and 2-hexanone).

Results and Discussion

PTR-ToF-MS allowed the successful detection of a great number of mass peaks corresponding to different groups of VOCs present in dairy products such as aldehydes, ketones, diketones, carboxylic acids, terpenes and sulfur compounds (Figure 1a). In most cases the distinction of isobaric VOCs mass was achieved (Figure 1b).

PTR-TOF-MS monitoring and modeling of volatile evolution during fermentation

Figure 2 shows the evolution of acetaldehyde and diacetyl during the incubation process of full, low and non-fat milks. Acetaldehyde and diacetyl belong to the volatile compounds that are found in high concentration in fermented milks and that are directly related with their refreshing/buttery aroma. Other compounds with major impact on the formation of aroma of fermented milks can be also tentatively identified such as 2-propanone, 2-butanone, acetoin/butyric acid, ethanol and 2.3-pentanedione. VOCs evolution during the fermentation process indicates: a) a sigmoidal trend, similar to that of lactic acid bacteria growth during incubation, for acetaldehyde, diacetyl, acetoin/butyric acid and 2.3-pentanedione, b) the physicochemical (acidification) and colloidal (destabilization of casein micelles, formation of casein-whey protein linkages, gelation phenomena) changes seem to affect the release of the VOCs in the headspace as depicted by the reaching of a concentration plateau in the range of pH 5-5.4 (gelation region), c) a depletion for several VOCs as formic acid and 2-propanone depending on the milk base characteristics.

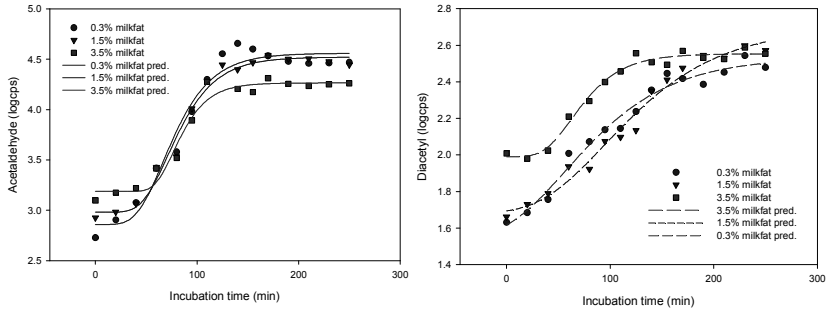

Figure 2: Evolution of acetaldehyde and 2,3butanedione (diacetyl) during the incubation of fermented milks with different fat levels. Experimental data and modified Gompertz model fitting.

Considering the shape of the VOCs evolution curves and the biochemistry of the fermentation process the experimental data were fitted in the modified Gompertz model which has been previously applied for the description of the pH (De Brabandere and De Baerdemaeker 1999) and viscosity changes (Soukoulis et al., 2007):

PTR-TOF-MS monitoring of milk base impact on the release of endogenous VOCs in yogurts

Acetaldehyde was significantly ($p<0.001$) higher in the low fat – unfortified systems (6.15±0.48 and 5.6±0.60ppmv respectively). A similar trend was also reported in the case of 2-propanone (0.91±0.11 and 1.13±0.07ppmv), diacetyl (334±37 and 350±34 ppbv), 2,3-pentanedione (54±6 and 55±6 ppbv) and 2-butanone (56±7 and 68±5 ppbv) for the same systems In contrast, the concentration of flavor compounds in the headspace with hydroxyl groups (ethanol and acetoin)

In the case of stirred yogurts, the gel breakdown did not induce significant changes in the headspace concentration of the most compounds, with the exception of ethanol, acetoin and 2,3-pentanedione being significantly ($p<0.05$) higher in the stirred yogurts (267±29, 153±11 and 38±1 ppbv respectively) than set style ones (232±19, 134±9 and 45±3 ppbv respectively).

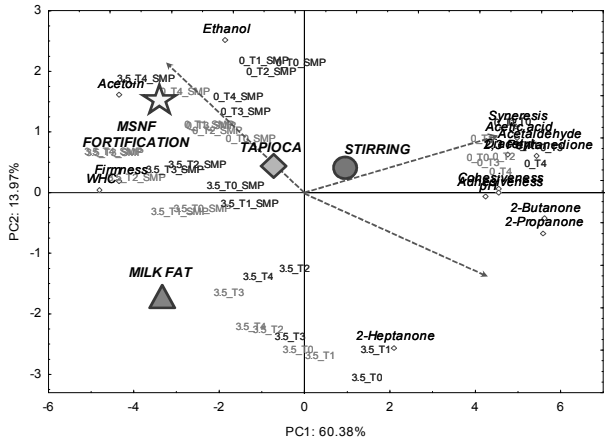

Figure 3: First and second dimensions of principal component analysis on the flavor compounds, textural, physicochemical and compositional data of the yogurt samples. T0 – T5: modified tapioca starch added in different levels (0 – 2.0%), SMP: samples fortified with skim milk powder, 0 and 3.5: milk fat concentration, with blue color are signified the stirred style yogurts and with green color the set style ones. The arrows depict the chemical affinity (acetaldehyde – diketones, ketones and hydroxyl group containing compounds) of the volatile compounds as they determined in the headspace.

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Applications of PTR-ToF-MS on Coffee

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Abstract

Over the last decade, PTR-MS has made major contributions to the progress in coffee research. The research group on "Analytic and Analytical Technologies" at the Zurich University of Applied Sciences in Wädenswil, has established over the last two years a strong research focus on the science of coffee. In this frame, PTR-ToF-MS is used in concert with complementary analytical technologies, to address applied research projects.

Here we report on a series of on-going projects, where PTR-ToF-MS plays a significant role. We outline how PTR-ToF-MS data are being integrated into extensive analytical studies, to achieve a more comprehensive understanding of the subject under study. This includes (i) fundamental investigations on the temperature dependence of partition coefficients of volatile flavor compounds (ii) on-line process monitoring and (iii) the development of a predictive model for coffee sensory profiles.

Detection and Monitoring for Safety, Security and Industry

Detection and Monitoring for Safety, Security and Industry using PTR-MS

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Abstract

PTR-MS technology has many advantages as an analytical tool (e.g. real-time analysis, no sample preparation, very low detection limits, high selectivity and very short response time), making it an ideal technology for many applications. Predominantly, the focus of use has been in the areas of atmospheric, environmental, food and (to a lesser extent) health sciences. However, PTR-MS is one of the few instruments that is extremely broad-based in terms of its analytical capabilities. New developments by Ionicon Analytik GmbH, including switchable reagent ions, improved mass resolution, improved sensitivity and direct aqueous injection have greatly extended these capabilities, not only for the main-stream areas mentioned above, but also for completely new fields of application. In this presentation we will discuss the applications of PTR-MS to Industry and Homeland Security, with particular focus on threat agent (explosive, chemical warfare agent and illicit drug) detection. Whilst there have been a number of studies on PTR-MS and its use in Homeland Security presented in the literature, there is very little on industrial applications. However, potential applications may be found by reviewing the use of another drift-tube based technology, Ion Mobility Spectrometry (IMS), known best for screening explosives at airports and detecting chemical agents for the military, and other analytical instruments (e.g. GC-MS) for industrial purposes. With regards to IMS, when operating in DC mode, it may be regarded as a high pressure PTR chamber. Therefore, basically, PTR-MS can be used for anything that IMS in positive ion mode can detect, although it is important to note that the reverse is not true owing to the more complex reagent ions used in IMS systems.

Introduction

The failed terror plot to transport printers containing the explosive pentaerythritol tetranitrate, or PETN, from Yemen to Chicago synagogues in October 2010 once again focused attention on the need to detect explosives reliably and in real-time. PETN is the same explosive that the so-called "shoe-bomber" tried to set-off on an American Airlines jet to Miami in 2001, and was involved in the failed attempt at setting off a bomb on an airliner in midair (Northwest Airlines Flight 253, 25th December 2009) by the Nigerian born Umar Farouk Abdulmutallab. PETN is an extremely powerful explosive, belonging to the nitroglycerine family, but is very stable. It is therefore a

preferred explosive used by terrorists. A major problem for security personnel is that PETN is difficult to detect, even "sniffer" dogs have problems in its detection.

Often, when dealing with the extremely low vapour pressures such as those that are associated with solid explosives and drugs, spectrometric analytical techniques rely on the detection of volatile chemical markers present or added to the compound rather than the compound itself [1]. In PTR-MS the parent molecule is targeted. Providing the protonated parent results from the reaction processes occurring within the drift tube of a PTR-MS, then when monitoring a complex chemical environment for threat agents this leads to a higher level of confidence in their detection, and hence a potential reduction in the chances of false positives when applying PTR-MS to real-world situations. This highlights a major advantage of PTR-MS. However, we mention that whilst analytically the PTR-MS is most useful when the protonated parent is produced and detected, proton transfer does not necessarily proceed non-dissociatively, as we have recently demonstrated for a series of saturated alcohols [2].

Of course, given the importance of threat agent detection for our society, several detection technologies have been and are being developed. Most notable of these is Ion Mobility Spectrometry (IMS), which collects and analyses minute quantities of particle contamination [3]. Despite its sensitivity and robustness, IMS has the disadvantage of limited chemical specificity as a result of its low temporal resolution inherent in the separation of the ion mobility peaks. This can cause false positive signals resulting from the erroneous identification of harmless interferents as a threat agent. PTR-MS, and in particular the high mass resolution PTR-TOF 8000 (Ionicon Analytik GmbH), has the potential of detecting traces of threat agents in ambient air, and adhered to people or objects, with a higher level of confidence (low rate of false positives) than available with IMS providing the protonated parent ion is observed.

In a collaboration involving the Universities of Innsbruck, New York, and Birmingham and the Innsbruck-based spin-off company, Ionicon Analytik GmbH, we have been investigating the potential of PTR-MS for the detection of explosives [4] and other threat agents including chemical warfare agents [5] and drugs [6]. In the presentation, we will review all PTR-MS studies of explosives, including the liquid explosive TATP [7] and solid explosives [4, 8], including dinitrobenzene (DNB; 1,2, 1,3 and 1,4, $C_6H_4N_2O_4$), 1,3,5 trinitrobenzene (TNB, $C_6H_3N_3O_6$), RDX, TNT, HMX, and PETN, $C_5H_8N_4O_{12}$), in addition to the general purpose plastic explosive Semtex A (containing 6% RDX and 94% PETN), chemical warfare agents (e.g. sarin and mustard gas [9]) and simulants [5], and drugs; N-methyl-3,4-methylenedioxyamphetamine (ecstasy), morphine, codeine, cocaine, and heroin [6]. Although an objective of the presentation is to review current and potential applications of PTR-MS in the industrial context, in this paper we just present some of our results from our recent studies involving threat agents.

Experimental Methods

The majority of the data presented in this paper were obtained with a PTR-TOF 8000 instrument (Ionicon Analytik GmbH [10]). A detailed description of the newly developed PTR-TOF 8000 can be found in a previous publication [11] and therefore only a brief discussion of the experimental procedure is presented here. The uniform heating of the inlet lines and PTR chamber was critical to the measurements involving the solid explosives and drugs because of their condensable nature. To sample and analyse the headspace above the explosive and drug threat agents used in this study and to allow for any background signals, the following procedures were adopted. Initially laboratory air was drawn through a charcoal filter (Supelco Supelpure HC 2-2445-U) into an empty glass vial through a septum in the lid via an inlet line of $1/16^{th}$ inch PEEK (internal diameter 1mm, VICI AG International). An outlet line, which also passed

through the septum, of the same PEEK tubing as the inlet, was then connected to the analyte inlet of the PTR-TOF 8000 via a heated inlet line. A background spectrum was then recorded. Following this the vial was opened and a small amount (approximately 50 mg) of a threat agent was placed inside. The vial was then sealed and kept at room temperature. Air was again introduced into the vial via the inlet line after passing through the charcoal filter, but this time passed over the explosive/drug sample before passing out through the outlet line to the PTR-TOF-MS for analysis. As soon as conditions had stabilized, i.e. the protonated parent ion signal was no longer increasing with time, mass spectra were once more recorded. Comparisons between the background spectra and those with the analyte were then made to determine the product ions resulting from the reaction of H_3O^+ and a given drug. To record the VOCs emitted from the CWA simulants at room temperature, a small droplet of a particular simulant was placed into a closed glass vial. Given the volatility of the simulants, the volatile concentration entering the PTR TOF 8000 instrument had to be drastically reduced in order to simulate 'real-life' conditions. This was achieved by rinsing the glass vial several times in distilled water, drying the glass vial so that only a residual of the simulant remained, and then sealing the vial.

Results

There are two important areas involved in the detection of explosives:

- *Forensics* – the identification of explosives on suspects' hands, clothing and other items
- *Environmental* – analysis of explosives in soil and water.

In terms of forensics, an important aspect of using the recently developed PTR-TOF 8000 for threat agent detection is its high mass resolution, which leads to a high confidence in detection. This is exemplified in figure 1, which shows the result of a measurement of a small block (approx. 8 grams) of TNT placed directly in front of the PTR-MS inlet. For this experiment, the inlet line was not modified, i.e. the first 2-3 cm were not heated, which results in condensation of the TNT vapor on surfaces and subsequently a much slower signal response/signal increase than could be obtained with a perfectly heated inlet line without cold spots. However, the quintessence of figure 1 is that there is an unidentified lab-air compound present at the same nominal mass as TNT. With the mass resolution of about 8,000 m/Δm this compound can be clearly separated from TNT, thus effectively suppressing the risk of false positives.

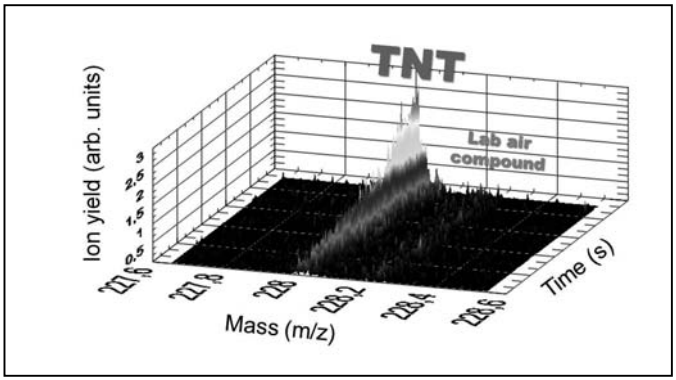


Figure 1: Separation of TNT and a harmless lab-air compound with the PTR-TOF 8000.

For the environmental aspects of explosive detection, we applied the newly developed direct aqueous injection (DAI) technique [12] to the detection of TNT in water. The DAI technique is invaluable for the detection of trace substances in water that have high Henry coefficients, i.e. for those compounds which are extremely difficult to detect via their headspace. Explosives fall into this category, and are extremely toxic (e.g. TNT poisoning can lead to aplastic anemia or toxic jaundice). For decades obsolete explosives and munitions have been either buried in the ground or dumped at sea. There is therefore an urgent need for on-site detection and identification of traces of explosives in areas suspected of being contaminated by explosives. An obvious application is monitoring the quality of groundwater. To illustrate the potential of PTR-MS for this kind of work, approximately 1 mg of TNT was placed in a vial containing 50 ml water without stirring, shaking or heating. Samples of the water were taken and injected into the PTR-MS via the DAI system over a period of several months. Figure 2 provides a summary of the results. It can be seen that even after one night sufficient TNT could be detected in the water, although TNT is practically insoluble in water. With time, the concentration of TNT in water increased and reached a "saturation" level after approximately two months.

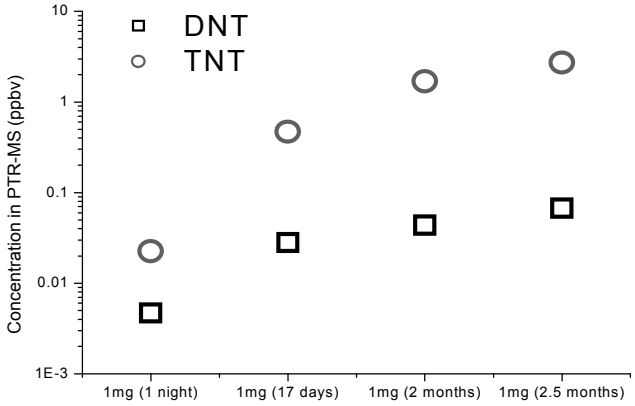
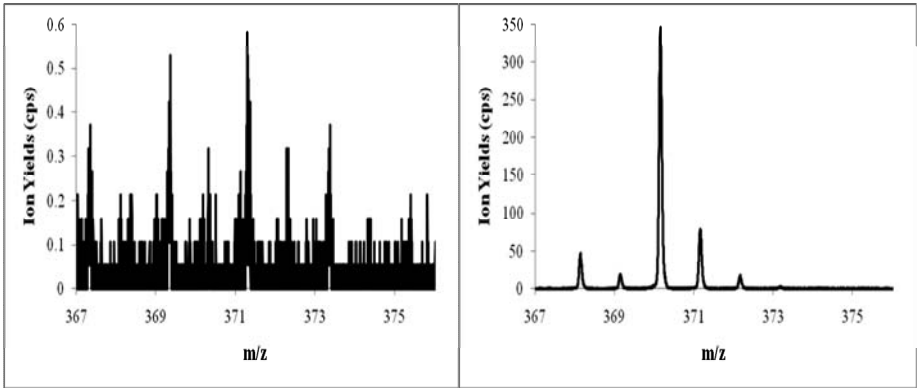


Figure 2: Analysis of TNT concentration in water as a function of time. (DNT is found to be an impurity in our TNT sample.)

In addition to TNT, we have also demonstrated that the nearly unambiguous detection of threat agents is possible for all common solid explosives (RDX, PETN, HMX, etc.), and other threat agents, including chemical warfare agents (mustard gas and numerous CWA analogues) and illicit and prescribed drugs (heroin, cocaine, morphine, ecstasy, etc.) via direct headspace sampling at room temperature. Figure 3 illustrates this for heroin.



(a) (b)

Figure 3: PTR-TOF 8000 analysis of the headspace above heroin placed in an enclosed environment at room temperature. (a) refers to the spectra obtained for purified laboratory air passing through an empty vial and (b) corresponds to the spectra recorded using the same vial containing heroin. The protonated parent drug molecule is at m/z 370.17. This figure does not only illustrate the low background signals, but again demonstrates the usefulness and importance of the high mass resolution separating the protonated parent from any background peaks.

Concluding Remarks

Studies on explosives [4, 9], chemical warfare agent simulants [5, 8], and drugs [6] have shown that PTR-MS is capable of providing a reliable analytical detection method for a broad range of threat agents, which is simple, rapid and extremely sensitive. Further technological developments are needed in order to demonstrate the application of the PTR-MS technology in "real-world" environments when interferents could be present that result in an ion with an *m/z* close to or at that of a threat agent. However, the successful detection of the protonated parents for threat agents, as illustrated in this paper, warrants the further research and development required to provide a sampling system which would provide fast recovery times (e.g. tens of seconds) in order to eliminate possible memory effects.

Acknowledgement

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Analytical detection of illicit, prescribed and designer drugs

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Abstract

Due to the major societal problems associated with narcotics abuse, the detection of illicit substances is currently an area of major research interest. Here we report the use of Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) for the detection of illicit, prescribed and designer drugs: ecstasy (N-methyl-3,4-methylenedioxyamphetamine), morphine, codeine, cocaine, heroin, ethcathinone, 4-fluoroamphetamine, 2C-D and dimethocaine. We describe the capabilities of the instrument by the direct sampling of all the drugs through headspace above small solid quantities (approximately 50 mg), placed in glass vials at room temperature, i.e. without heating and pre-concentration of the sample. As required for analytical purposes, the protonated parent was observed for all of the drugs. However, in addition other channels were observed than the non-dissociative one. The fragmentation behavior is discussed.

Introduction

Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) has developed into a promising and powerful tool for the detection of threat agents [1-4], including explosives [1, 2], chemical warfare agents (CWAs) [3] and most recently drugs [4]. PTR-TOF recently developed by Ionicon Analytik GmbH [5] features excellent mass resolution (m/Δm of 8000) and high sensitivity (~ 50 counts/sec (cps) per 1 ppbv of trace compound concentration at 10^6 cps of H_3O^+ reagent ion signal). Here, we report the use of PTR-TOF-MS, to the detection of illicit, prescribed and designer drugs, namely ecstasy, morphine, codeine, cocaine, heroin, ethcathinone, 4-fluoroamphetamine, 2C-D and dimethocaine.

One of the most notable technologies for the detection of illicit substances is ion mobility spectrometry (IMS), which collects and analyses minute quantities of particle contamination [6-14]. Despite the advantages associated with the use of IMS to detect illicit substances, there are also disadvantages that can be of considerable importance in many applications. IMS has the disadvantage of limited chemical specificity as a result of its low temporal resolution inherent in the separation of the ion mobility peaks. This can cause false positive signals resulting from the erroneous identification of harmless interferents as a threat agent.

Experimental Methods

All of the data presented in this paper were obtained with a PTR-TOF 8000 instrument [5]. For the detection of drugs, the following parameters and procedure were used: the operating pressure in the drift tube was kept at 2.3 mbar and the drift temperature was kept at 110°C to reduce memory effects. The inlet temperature was maintained at 140°C to minimize surface adsorption. We varied the drift tube voltage from 400 to 1000 V such that the corresponding ratios of electric field strength (E) to molecular density (N) – often referred as reduced electric field, (E/N) - varied from 90 to 220 Td (1 Td = 10^{-17} Vcm^{-1}). For detection of the drugs, first laboratory air was drawn through a charcoal filter (Supelco Supelpure HC 2-2445-U) into an empty glass vial through a septum in the lid via an inlet line of $1/16^{th}$ inch PEEK (internal diameter 1 mm, VICI AG international). Then the same air was drawn into the heated inlet line of the PTR-TOF 8000 and a background spectrum was recorded. Following this the vial was opened and a small amount (approximately 50 mg) of a drug was placed inside, and then again the vial was sealed. Exactly the same experimental set-up was used for the sample as for the background measurement and the sealed vial was always kept at room temperature. As soon as conditions had stabilized, i.e. the protonated parent ion signal was stable; mass spectra were once more recorded. Then a comparison of the background spectrum and those for the sample was made in order to determine the product ions resulting from the reaction of H_3O^+ and a given drug.

The illicit drugs used in this study were purchased from Serobac Labordiagnostika, Handelsgesellschaft m.b.H., for which we applied for a license and then received it from the Magistratsabteilung V Gesundheit, Markt- und Veterinärwesen of the city of Innsbruck, Austria and all these drugs had certificated stated purities greater than 99% (as calculated from the distribution of 6 HPLC analyses with a 95% level of confidence by the company Lipomed GmbH) and the legal designer drugs were purchased via the internet.

Results and Discussion

An important feature of the PTR-MS is its soft ionization technique which leads to the production of the protonated parent ion and hence identification of the drug with a very high level of confidence [4]. It's possible to detect and measure all of the above mentioned drugs using PTR-TOF. Along with this, we also performed E/N studies over a range of approx. 80 to 220 Td for all of the mentioned drugs. Usually, parent ion decreases with E/N and the observed fragments increase with E/N [1, 3]. Figure (1) shows as an example, the mass spectra obtained from the sampling and analysis of (a) background and (b) headspace above MDMA, obtained from the summation of nine scans each with a two second integration time, over a small m/z range, which covers that of the protonated parent, at 120 Td. Fig. (1c) shows the chemical structure of MDMA. The clear difference in Figs. (1a) and (1b) shows the sensitivity of PTR-MS instrument to detect the MDMA at room temperature without the need for pre-concentration, which is often required for drug detection using IMS.

For MDMA, the most dominant ion seen is the protonated parent ion (m/z 194.12). We also observed an ion at m/z 212.12, which is either an addition of water onto the protonated parent or formed through stabilization of the complex ($M.H_3O^+$), i.e. the association of H_3O^+ with the M (here M is used to present the MDMA). This was the only drug for which we observed a $M.H_3O^+$ product. The reason for this is the presence of a secondary amine group in the chemical structure of MDMA. We also found two main fragments for MDMA at m/z 192.10 and m/z 163.08, corresponding to the loss of molecular hydrogen (H_2) and methylamine (CH_3NH_2), respectively.

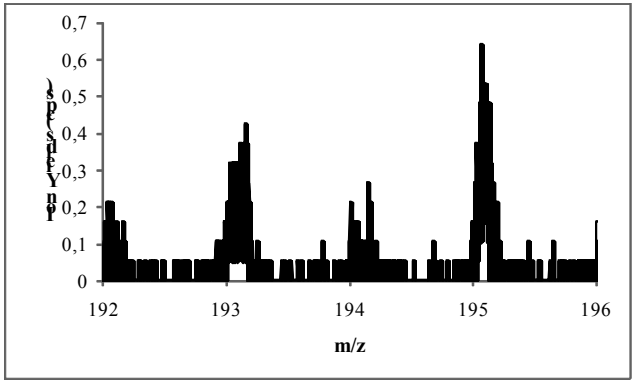

Figure 1a: Background spectrum

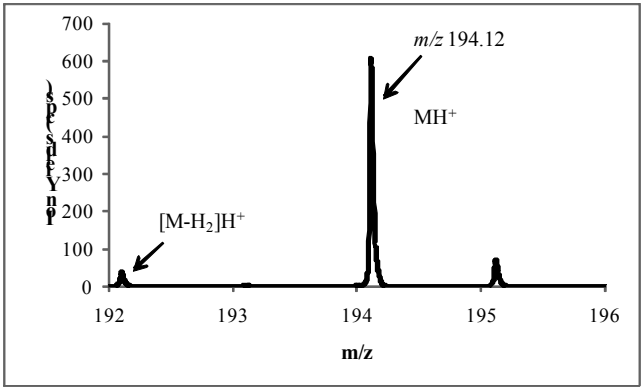

Figure 1b: Sample (MDMA) spectrum

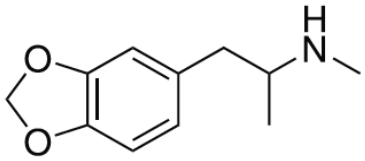

Figure 1c: Chemical structure of MDMA

Acknowledgements

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Detection of trace compounds in industrial waste liquids

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Abstract

Although PTR-MS is an outstanding technology for trace gas analysis, it has one drawback: volatile organic compounds solved in liquids can only be measured via headspace analysis or membrane inlet setups. Both sampling methods are suitable for certain applications, but suffer also from a number of disadvantages.

The direct aqueous injection (DAI) technique which we present here turns out to be an ideal solution for direct analysis of liquid samples with PTR-MS. For proof-of-principle measurements solutions were prepared with 1 to 1000 ppbw (part per billion weight) of methanol, acetonitrile, pyridine (additional mixtures down to 125 pptw were prepared) and cyclohexanol in distilled water to find the best injection parameters. In order to demonstrate a possible field of application we present here measurements of traces of the solid explosives TNT and DNT in water.

Introduction

PTR-MS is a well established technique for online quantification of volatile organic compounds (VOCs) in air. However, one disadvantage of PTR-MS is that trace compounds in water can only be investigated via headspace measurements above the liquid's surface. The Henry constant gives the relation between the concentration of a substance in the liquid to the concentration in the headspace, i.e., substances having a very high Henry constant are extremely difficult to detect in the headspace and must be present in very high concentration in the liquids to be detectable in the gas phase above the liquids [1]. Boscaini, Alexander et al. overcame this problem by developing a membrane inlet (MI) system for PTR-MS [2,3]. They published detailed studies on VOCs in water using this MI mass spectrometry setup. However, using a membrane to introduce VOCs from liquids into PTR-MS has several considerable disadvantages, e.g. selectivity of the membrane, low sampling speed and cross-contaminations when changing the sample. Therefore, in the present work we demonstrate the feasabilty of a different approach, namely direct injection of water into an airstream prior to sampling this air by PTR-MS. This has several advantages, i.e. (i) no pre-treatment of the sample or pre-concentration, (ii) minimized losses of volatile analytes, (iii) fast response times, etc.

Assuming that the injected liquid is evaporated completely in the carrier air flow and that the gas volume per time unit originating from the evaporating water is negligible compared to the carrier airstream, we can write for the concentration C_{PTR} (volume concentration), which we measure with the PTR-MS Instrument:

$$C_{ptr} = \frac{C_w \cdot l}{f_{air} \cdot M_w} \cdot V_{mol}$$

where C_w is the concentration of the dissolved compound in water (mass fraction) to be determined, l is the liquid flow rate ("injection rate"), f_{air} is the flow rate of the carrier airstream, M_w is the molecular weight of the dissolved compound and V_{mol} is the molar volume.

In this presentation we demonstrate proof-of-principle investigations of direct aqueous injection (DAI) coupled with PTR-MS and show first results obtained for methanol, acetonitrile, pyridine and cyclohexanol contained in water matrices. Furthermore an application of the system for the detection of explosives in liquids will be demonstrated.

Experimental Methods

In Fig.1 a schematic illustration of the present direct aqueous injection (DAI) inlet system is shown. The carrier airstream is generated by a diaphragm pump. Afterwards it passes through an activated charcoal filter to clean the air. To stabilize the humidity a cooling trap (0–4 ◦C) is used. Thereafter the exact amount of clean and dry air entering the injection region is adjusted by a mass flow controller and subsequently heated in a thermostatic heating box to ensure that all parts (tubes, fittings, connectors, etc.) are at the same temperature, so that no condensation on cold spots can occur. The temperature can be chosen depending on the samples. The needle of the syringe is pierced through a "marathon septum" which seals one of the openings of a T-piece. The T-piece is mounted directly into the carrier gas line. The injection speed is controlled by a high precision syringe pump (Nemesys, Cetoni). A second T-piece serves as a connector to the PTR-MS instrument and acts as a bypass for the excess airstream which is not introduced into PTR-MS (typical airstream in the DAI system: 1000–2000 sccm; typical amount of air sampled with PTR-MS: 100 sccm).

For the present studies a high sensitivity (HS) PTR-MS instrument (Ionicon Analytik) was used, since it has proved to reach a detection limit below the pptv level [4]. For the proof of principle measurements solutions were diluted with water to 1–1000 ppbw (part per billion weight: µg/l) of methanol (Wako Chemical), acetonitrile (Sigma–Aldrich), pyridine (Sigma–Aldrich; additional mixtures down to 125 pptw were prepared) and cyclohexanol (Sigma–Aldrich). Because of the low water solubility of cyclohexanol (36 g/l at 20 ◦C), 1ml of cyclohexanol and 1ml of water were mixed in a glass bottle and shaken for 1 h. As a stock solution 300µl were diluted in 10 ml of water, whereas the other well soluble chemicals had a starting solution of 1 g/l. For dilution simple distilled water (Brenntag CEE) was used.

Furthermore in a further step of development the real-time detection of solid high explosives in water with DAI was investigated. We prepared solutions of explosives in two ways. In the first procedure we just put two 1-mg pieces and one 44 mg piece of TNT into a 50 ml water vial at room temperature without shaking or stirring and measured them after certain time intervals (one day to two months). The second procedure was dissolving a specific amount of pure DNT in water by mixing and stirring in order to prepare a solution with well-defined concentration.

The PTR-MS instrument was operated at standard conditions (reduced electric field strength approximately 130 Td). The temperatures in the PTR-MS were 70 ◦C for the inlet-tube and 80 ◦C for the drift-tube. In each experiment background signals were measured. Subsequently, the

sample was injected and measured for 20–30 min to check the stability and exclude any fluctuations.

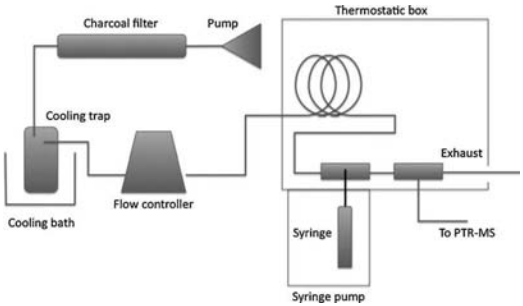

Figure 1: Schematic drawing of the DAI inlet system.

Results

The most important parameter of the new DAI injection system is the ratio between the airstream (air flow in l/min) and the injection speed (liquid flow in µl/s). By varying the airstream and keeping the liquid flow constant (0.1 µl/s) we could see a nice linearity down to 0.5 l/min where droplet formation starts. Consequently we chose 1.75 l/min for further measurements, during which we changed the injection rate. The data were linear until droplets were formed (about up to 1 µl/s).

The most important result of the proof-of-principle measurements is that the correlation between the concentrations of methanol, acetonitrile, pyridine and cyclohexanol measured by PTR-MS is linear over several orders of magnitude for different liquid concentrations. It can also be seen that the detection limit lies at about 100 pptw.

The measurements of the solid explosive pieces provide evidence that we can detect even very small traces of TNT and DNT in water. The concentration increased rapidly the first two days after the pieces of TNT had been placed in the water, whereas after two months the concentration approached saturation. The 1-mg TNT pieces were dissolved completely after 2 months. Furthermore the water becomes a bit pinkish, which could be a possibly sign of photolytic degradation reactions [5].

The correlation of the DNT concentration from the PTR-MS measurements versus those in the liquid sample is linear over several orders of magnitude, down to the concentration of around 300 pptw. So we can assume that the detection limit for DNT is at least in the range of several hundreds of parts per trillion by weight (for an integration time of about 5 min). However, this detection limit is dependent on the molecular mass of the sampled compound.

Discussion and Conclusions

We conclude from this proof-of-principle measurements for the new direct aqueous injection system (DAI) that the ideal injection conditions for most of the substances are 1.75 l/min for airstream and 0.6 µl/s for injection rate. With these parameters we can reach a detection limit of about 100pptw and a response time of 20s.

The detection of solid explosives in water provides evidence that we are able to detect traces of explosives in water in low concentrations. Furthermore we could confirm linearity between the concentrations measured by PTR-MS and concentrations in the prepared liquid solutions of DNT.

Some of these results concerning methanol etc. have been described in more detail in [6] and some of the results for explosives will appear in [7].

Acknowledgement

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Measurement of AMC (Airborne Molecular Contamination) in High Purity Production Environments and Cultural Heritage Institutions

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Abstract

Proton Transfer Mass Spectrometry (PTR-MS) is a viable technology to perform trace contamination measurements and monitoring tasks in high purity environments. These can be clean rooms and minienvironments of the semiconductor industry as well as clean and sealed showcases in cultural heritage institutions.

On both applications the strengths of the technology – fast on-line quantification of highly fluctuating compounds concentrations at low demands on sample flow and volume – are crucial parameters for successful assessments.

We are presenting examples from process environment control measurements that have been performed to examine the root cause of a severe process disturbance by the identification of the contaminant and its time depending behavior.

Moreover we show examples of a micro-invasive method of contamination assessments of museum showcases made in various designs and materials and containing diverse display materials meant to inspect whether preventive conservation target levels for objects storage are met.

Introduction

Trace contamination measurements are a necessity for a wide range of applications where the air or gas purity is of crucial importance for the quality or yield of a product or the unchanged preservation and keeping of either production master tools or cultural heritage objects. In some applications the continuous and uninterrupted supply of clean gas or clean air is so important that periodic measurements are more and more replaced by continuous on-line measurements – called monitoring. This is the more the case for e.g. semiconductor production as recent findings have shed a light on the dramatic fluctuations of the concentration of so called AMC (Airborne molecular contamination) and the effects of short excursions to the product yield. For storage of precious objects in semiconductor manufacturing as well as in archiving or exhibiting objects of cultural significance it is necessary to establish whether standards are met from a minimal sample volume. This is a requirement since the storage containers are to be kept sealed at all times, even during sampling, in order to prevent an unwanted exchange between the inner and outer container environment.

PTR-MS as a technology combining fast response at low detection limits and flexible adaptation capabilities to the tasks is a perfect technological base and has therefore been chosen by our company to be applied in numerous of our contamination control projects.

Experimental Methods

All measurements have been performed with a prototype of the AMC C-1000 monitor jointly developed by Ionicon Analytik GmbH, Innsbruck and artemis control AG, Uster. The AMC C-1000 monitor is based on the instrumental backbone of a PTR-MS compact instrument. This means it is a unit consisting of an ion source and ionization chamber in the H_3O^+ mode, a quadrupole mass separation section and a channeltron ion registration unit.

All measurement have been performed at operation parameters typical for the compact PTR-MS, e.g. a sample flow to the ionization chamber of 5 ml/min and standard conditions for e.g. ion source conditions and detector voltages.

The set-up, design and tuning of the AMC monitoring software are specific for the AMC C-1000 monitor. This software package enables direct readings of concentrations per target compound to be displayed and stored on an internal display and computer. Specific typical cross-interferences of compound mixtures and other compounds present besides the target analytes are taken care of and are compensated by intelligent algorithms that are run on a variety of masses detected during a measurement cycle. The set-up of these monitoring routines requires input data on the component mix in the environment and are obtained by other techniques such as Tenax/TD-GC-MS before the monitoring. Clearly the applicability of the parameter settings of the monitoring program has to be addressed and checked before the start of extensive on-line monitoring campaigns and requires expert know-how. However, the structure of the monitoring hard- and software enables us to fine-tune the measurement program and result evaluation in case of strongly deviating conditions from the standard ones.

With the hardware and software used for the AMC C-1000 monitor detection limits per compound of 0.2 to 0.6 ppb_v could be achieved. These detection limits are based on the results of a multi-component monitoring setting and represent the 2-sigma signal readings of operation on ultrapure/zero air. A typical cycle time for the monitor is 40 sec for a complete measurement cycle of 5-7 target compounds.

Details can be found visiting the page www.amc-monitor.com

Measurement of contamination in a semiconductor clean room environment

The measurements performed in semiconductor clean room environments strived to identify origins of process emissions that occurred periodically but unexpected in the clean room atmosphere. Those process emissions did not impose a threat to health or the original process as the components are used as e.g. solvents in the processes themselves. However, solvents emitted constantly and unattended had been interacting with filtration devices meant to protect a critical and high purity process step. This interaction produced an unwanted by-product of the purification process that turned out to be a killer component for the process, in this case a DUV-photolithography. Although a solution for a modified, more tolerant purification device could be found [1] there was a clear interest to identify and stop the root cause for the unwanted solvent emission. For this task the capabilities of the AMC C-1000 monitor turned out to be crucial as the instrument is able to monitor unattended for 24 hours/7 days a week and its response time is

sufficiently fast (rise time one cycle, 45 seconds) to record the occurrence of peak emissions and to identify the underlying operation using the production- and machine log-files.

For those experiments reported the AMC C-1000 monitor was operated for the components *iso*-propanol, acetone, propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA) and acetic acid. The monitoring was continuous at one cycle per 45 seconds and lasted on specific positions several days. Results of those measurements together with tool-inside measurements are reported below

Measurements of contamination in museum showcases

Measurements in museum showcases have been performed to address the air quality in recently designed highly isolated and highly pure cases in comparison with so called "historic showcases" made from wood, painted decades ago but revarnished for use in a recent exhibition, and with showcases produced from MDF (middle dense fibre board). The latter can be regarded as a relatively common material in today's construction of showcases, as it allows to easily produce various object adapted cases on an economic basis given the variety of MDF materials on the market.

A general demand for display showcases is – besides the protection from theft - the isolation of the case interior from the climate variations in the museum rooms by annual or daily cycles due to seasons or visitor density. Moreover a rather complete isolation is regarded as protection from the intrusion of pollution and dust and thereby soiling of the objects.

On the other side preventive conservation standards pertain to the absence of potentially harmful components as inorganic or organic acids, e.g. acetic acid. Given the fact that showcase interior materials or objects themselves could be the emitting source, a thorough examination of a larger number of showcases in a major collection has been started.

The AMC C-1000 monitor was of help to perform this examination as it allowed in most cases the sampling line to access to the interior of the showcase by small service openings without opening the actual case. This supported both measuring the situation without dilution by room air as well as working on the showcases during opening times without security risk for the objects.

The monitor was programmed to record *iso*-propanol, acetone, 2-butanone, acetic acid, benzene, toluene and xylene with a cycle time of 15 seconds.

Results

The results for the screening of various semiconductor production tools of identical make in a production environment rendered conclusive results thanks to the fast time-resolved yet continuous recordings from the AMC C-1000 monitor It could clearly be identified that only 2 out of 20 tools had significant emissions during operation that contribute to nearly 100% of the total solvent load in the facility air. As those tools did not show emissions during idle times the solvent loss was not attributed to e.g. drop-loss from solvent reservoirs. It could be identified that an air extraction hose activated during wafer coating suffered from design failures and was the point of emission (see. Fig.1).

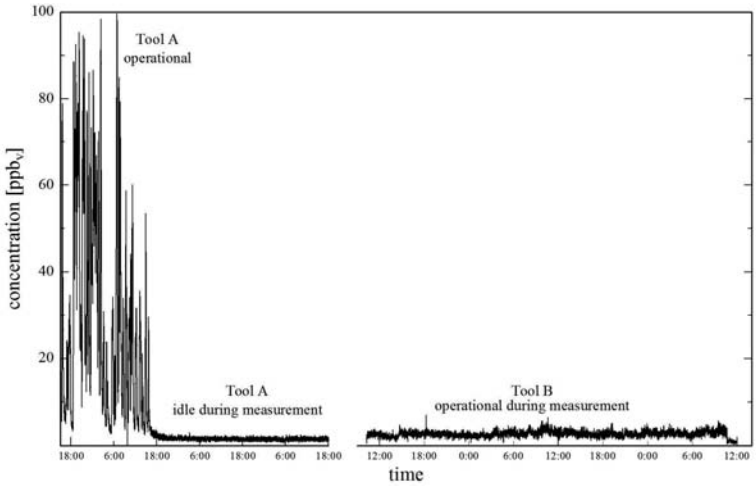

Fig. 1 Measurements of PGMEA in the basement of a semiconductor production facility using the AMC-monitor. The measurement positions of the sample line are the general downstream positions below the two different tools, about 1.2 m above basement level. Note the strong differences of Tool A "operational" and "at rest", compared to Tool B "operational".

For the examination of VOC-content in showcases of different make and design clear differences have been found mainly depending on the construction material and finishing procedures. Historic wooden showcases exhibited high levels of acetic acid which is known to emit from the wood even after long time. Levels of acetone and xylene turned out to be modest. Compared to that, the levels of acetone and xylene related to finishing are comparatively high in a newly designed MDF showcase for a temporary exhibition. This is accompanied by an elevated level of acetic acid in the same range as for solid wood material in historic display cases. This is consistent as such. Best conditions in terms of AMC have been found in the modern metal/glass type of displays. Consequently low levels of xylene have been quantified due to the lack of painting materials. Acetic acid and acetone are on a modest to low level and originate from the objects and support material (see Fig.2).

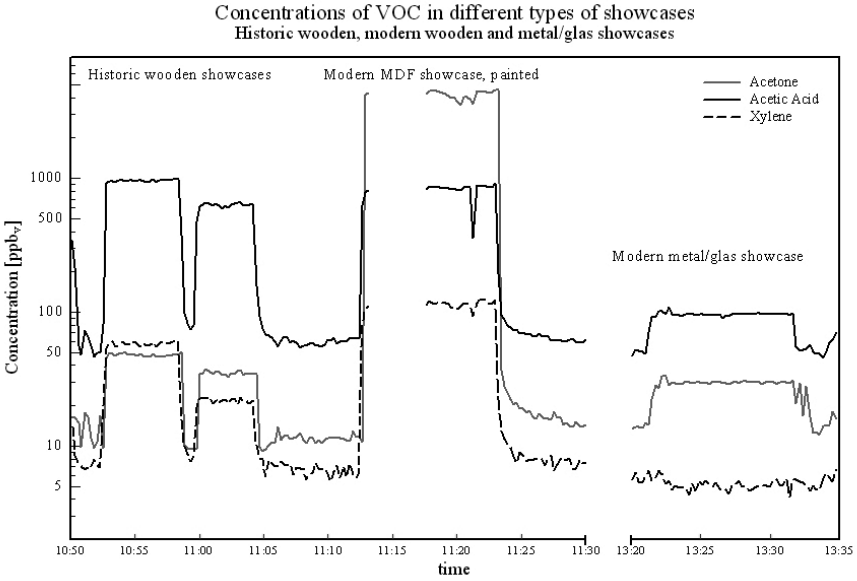

Fig.2 Results for acetone, acetic acid and xylene measured with the AMC Monitor inside showcases of various history and type. Note the varying concentrations of all components with the design material (log-axis). In the case of the comparison shown the material nature of the exhibited object is not influencing the concentration level

Discussion

PTR-MS in its further development state of AMC C-1000 monitor has proven to be a feasible technology to solve monitoring tasks that could not be addressed in the past mainly due to insufficient sampling and response time of other techniques. The capability to generate more and uninterrupted data from clean processes has recently even changed the understanding of defect generation in key production processes.

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Towards using artificial intelligence to detect anomalies in atmospheric mass spectrometry or other spectroscopic data

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Abstract

The real-time detection of low levels of unusual substances in everyday environments is an extremely useful capability in many environmental, health and security applications.

In many real-world scenarios, the target does not have a defined signature, and neither does the background against which this must be detected. In the worst-case scenario, one may not even know what one is looking for. In effect, one is looking for something which is "abnormal" appearing in the "normal" background.

Manually processing the data to look for the "needle in the haystack" is very inefficient and time consuming. Dstl has been leading a collaborative research programme seeking to develop artificially intelligent algorithms for detecting such anomalies. The algorithms are widely applicable to any sensor technique using two-dimensional data, including mass, mobility or optical spectroscopy.

Trace gas analysis of high purity gases using APCDI/MS and IMS/MS techniques

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Abstract

We have applied the Ion Mobility/Mass Spectrometry (IMS/MS) and Atmospheric Pressure Corona Discharge Ionisation/Mass Spectrometry (APCDI/MS) techniques to detect trace amounts of impurities in high purity technological gases N_2 and O_2. In the case of N_2 we have used positive ion mode to detect trace amounts of water and O_2. The main impurity in high purity O_2 was N_2 and its detection has been carried out in negative IMS/MS mode.

Introduction

Ion Mobility Spectrometry (IMS) is well known method for detection various types of impurities in the air [1] with high sensitivity and short response time. The main field of applications is in the fields of explosives and warfare detection [2] in last decades many new applications of IMS are explored [3].

In this paper we present the IMS/MS and APCDI/MS studies of the positive corona discharge in high purity Nitrogen and negative corona discharge in high purity Oxygen. We have measured the IMS spectra of the ions formed in corona discharge (CD) as a function of discharge current and the particular ion peaks in the IMS spectra have been identified using the MS. The time evolution of the ions formed in the corona discharge was studied using the APCDI/MS technique. Additionally, this work have demonstrated the ability of IMS and IMS/MS systems to detect trace amounts of H_2O, O_2 and NH_3 in Nitrogen down to 100 ppt and 10 ppt levels. In the case of Oxygen we were able to detect the Nitrogen traces in Oxygen at 500 ppb level. The detection limit is much lower; however, we were not able to obtain O_2 gas with better purity.

Experimental Methods

The IMS/MS (Figure 1) and APCDI/MS instruments equipped with point to plane corona discharge ion source were described in our previous work [4]. Two positive power supplies (Heinzinger) were used, one for corona discharge and one for the drift field. The electric field in IMS drift tube was 351,8 V/cm. In APCDI/MS experiment the electric field in the short drift region was varied in the range 6000-250V/cm with corresponding drift time of ions from 0.1 to 2ms approximately. The current of the corona discharge was varied from 3 to 10μA (limited by HV power supply) in case of IMS/MS studies, while in the case of APCDI/MS was at the constant value 10μA. The 6.0 Nitrogen and Oxygen (Linde) were further purified using MICROTORR getter traps. This technique reduced the concentration of O_2 (in the case O_2 we used trap without O_2 removal), H_2O, CO, CO_2, H_2 impurities under 100ppt and NH_3 and amines at 10ppt levels. The drift tubes of IMS/MS and APCDI/MS instruments were fed by Nitrogen or Oxygen at flow rate 900ml/min. The drift tube has been operated at atmospheric pressure and room temperature (294 K).

The quadrupole mass spectrometer (Pfeiffer Vacuum QMH 420) has been located in the vacuum chamber and differential pumping has been applied in order to achieve high vacuum in the vacuum chamber with mass spectrometer. The transport of the ions from IMS into vacuum has been facilitated via 100μm orifice. First vacuum chamber has been pumped by rotary backing pump down to pressure of approximately 10 Pa, the second vacuum chamber has been pumped by pair of turbomolecular pumps with overall pumping speed of 500 $l.s^{-1}$ and the quadrupole mass spectrometer has been additionally pumped by 70 l.s-1 turbomolecular pump.

The positive ions in the mass spectrometer have been detected by Secondary Electron Multiplier (SEM) using the single ion counting method. Using IMS/MS setup we were able to measure IMS spectra and mass resolved IMS spectra in both polarities. With open shutter grid mass spectra of the ions passing through the IMS has been measured. The APCDI/MS allowed us to measure time evolution of the ions formed in the corona discharge.

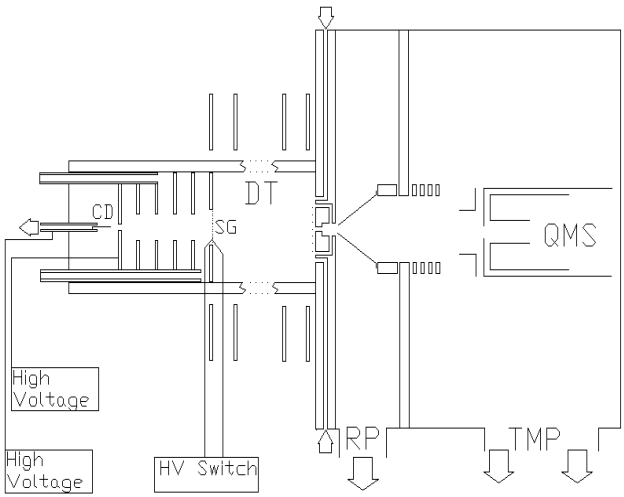

Figure 1: Schematic view of IMS/MS instrument with CD ionization source.

Results and discussion

Nitrogen

Three peaks with drift times 11.95 ms, 12.6 ms and 13.4 ms were observed in IMS spectrum using positive CD in pure N_2 at low discharge current of 3μA (Figure 2a). The corresponding reduced ion mobilities of these peaks are 2.42±0.05 $cm^2V^{-1}s^{-1}$, 2.3±0.05 $cm^2V^{-1}s^{-1}$ and 2.15±0.05 $cm^2V^{-1}s^{-1}$. The mass resolved IMS spectroscopy revealed that the dominant peak with reduced mobility 2.15 c $cm^2V^{-1}s^{-1}$ is composed of the ions H_3O^+(m/z=19), H_3O^+(H2O) (m/z=37) and $H_3O^+(H_2O)_2$ (m/z=55). The increase of the corona current resulted in increase of the peaks with reduced mobilities 2.42 $cm^2V^{-1}s^{-1}$ and 2.3 $cm^2V^{-1}s^{-1}$ and decrease of the peak with reduced mobility 2.15 $cm^2V^{-1}s^{-1}$ as can be seen from Figure 2a. In the Figure 2b we show the mass spectra measured at corona currents 3 and 10 μA. The mass spectra are dominated by $H_3O^+(H_2O)n$ clusters and with increasing corona discharge current m/z=30 and 18 (NO^+, NH_4^+ respectively). Precursors of these compounds are with highest probability formed in the positive corona

discharge. The formation of NO^+ could be thus used as a marker of the O_2 density in the high purity nitrogen. The formation of NH_4^+ is most probably with the presence H_2O in the nitrogen gas, however also traces of NH_3 impurities could be precursor of this ion.

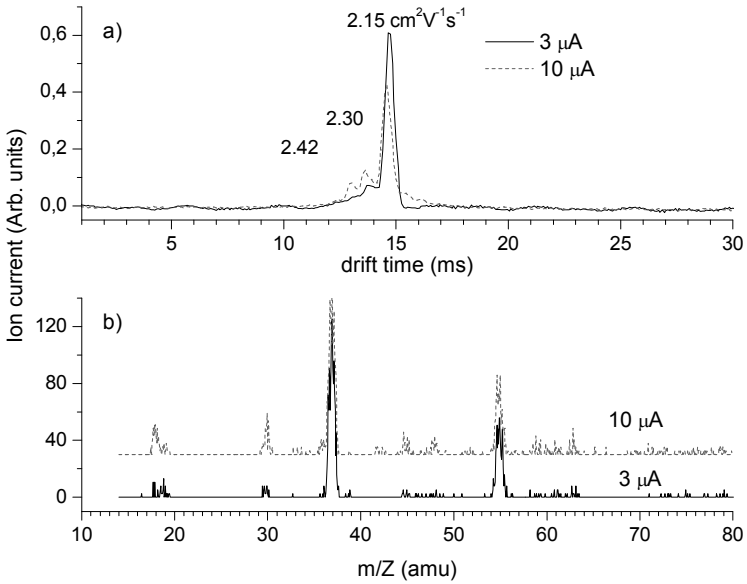

Figure 2: IMS spectra of positive ionsformed in positive CD in N_2 as a function of the corona discharge current, b) corresponding mass spectra.

Oxygen

The IMS spectra of negative ions formed in high purity O_2 (6.0 purity and further purified using Microtorr getter trap to remove organic compounds and water) show dependence on the CD current. At low discharge current, the IMS spectrum exhibits two peaks, the dominant one with reduced ion mobility of 2.51 $cm^2V^{-1}s^{-1}$ and second one 2.44 $cm^2V^{-1}s^{-1}$ (Figure 3a). With the increasing CD current the second peak disappears and the intensity of the first one increases. The corresponding mass spectra recorded under identical discharge conditions are presented in the Figure 3b. On basis of these mass spectra we have assigned the peaks in the IMS spectra. The dominant peak we associate with the m/z=60 and the second peak with m/z=32. On basis of the detailed analysis [1] the first peak we assign to $N_2O_2^-$ ions and the second peak to the O_2^-. This assignment has been confirmed also by mass resolved IMS spectroscopy. The existence of the $N_2O_2^-$ ions we link to the N_2 impurity in the O_2 gas. In 6.0 O2 there is according to the producers (Linde Gas) >0.5 ppm N_2. Unfortunately we were not able to further purify the O_2 in respect to N_2 due to inert character of nitrogen and we were not able to purchase O_2 of higher purity than 6.0. The formation of the $N_2O_2^-$ is result of the reaction of the O^- and O_3^- ions with N_2O formed in the negative corona discharge with traces of N_2. The O_2^- ions decays preferentially in ion molecule reactions with neutral O_3 efficiently formed in the negative CD in O_2.

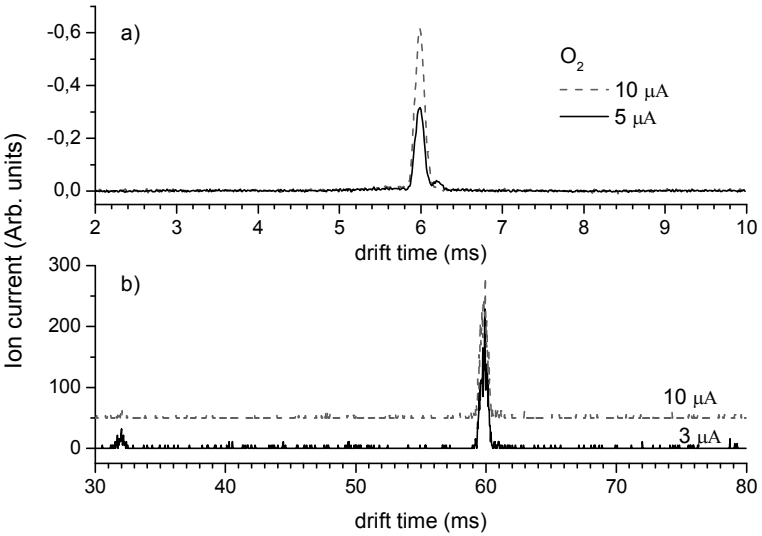

Figure 3: IMS spectra of negative ions formed in negative CD in O_2 as a function of the corona discharge current, b) corresponding mass spectra.

Acknowledgment

This work has been supported by This work was supported by the Slovak research and development agency projects LPP-06-0146, SK-CN-0015-09 and the VEGA grant No. 1/0051/08.

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Detection of Chemical Warfare Agents using Proton Transfer Reaction Mass Spectrometry

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Abstract

More than ever highly toxic and hazardous chemicals released intentionally or by acci-dent pose a significant threat for public life all over the world. The range of chemicals and chemical classes to be taken into consideration in this context is much more com-prehensive than it has ever been before.

Detection and Monitoring for Safety, Security and Industry

Regardless the fact that the Cold War period ended 20 years ago Chemical Warfare Agents (CWA) are still attractive for terrorists due to their high toxicity and disastrous impacts on casualties. Currently, analytical technologies like Ion Mobility Spectrometry (IMS) or Flame Photometry are made use of to design handheld CWA detectors and warning equipment in order to enable acting personnel to take measures of personal and collective protection in case of the appearance of CWA. Both technologies, how-ever, do not meet asymmetric threat scenario requirements comprehensively and pos-sibilities of technical improvement are limited due to physical regularities. In contrast classical Gas Chromatography–Mass Spectrometry (GC-MS) is a powerful mass selec-tive tool but not suitable to put handheld chemical detectors into practice and to detect chemical hazards in near real time.

Innovative analytical technologies are required to bridge the analytical gap between handheld detector technologies like IMS and GC-MS in terms of fast (near real time) detection, high sensitivity and high selectivity or information content respectively. Proton Transfer Reaction Mass Spectrometry (PTR-MS) has been considered to pose an appropriate technology to fit in the gap and fulfil all the aspects mentioned above.

Different PTR-MS systems (a PTR-quadrupole-MS, type “high sensitive” and a PTR-ToF-MS, both by IONICON, Innsbruck) were challenged with defined concentrations of a variety of chemical warfare agents.

Nerve agents like Sarin used at Tokyo underground in 1991 belong to the most hazardous agents and require the most demanding detection features. Conducting experiments with PTR-MS it was found that the different types of nerve agents tend to fragmentation depending on the systems adjustments whereas extremely stable ion species are formed at atmospheric pressure ionisation (API) conditions like in IMS usually. The systems adjustments were varied systematically and, further on, ammonia was used as a kind of ‘dopant’. It turned out that fragmentation of nerve agents can be suppressed and stable ion cluster species are formed under optimised conditions.

The investigations were extended to other CWA which are characterized by low proton affinity and formation of negative ions at API conditions primarily.

In conclusion it was found that PTR-MS methods are suitable to measure the broad range of Chemical Warfare Agents highly sensitive and in near real time. Compared to IMS mass information can be obtained from PTR-MS spectra what is an excellent start-ing point for

developing a recognition algorithm in order to detect agents automatically. In this respect PTR-MS may be considered as a bridging technology between IMS and classical GC-MS.

Roboter aided detection of threat compounds

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[*] *on leave from IONICON (Marie Curie-IAPP project no 218065)*

Abstract

From the beginning of 2008 until 2011 Ionicon was proud partner in the European Defence Agency JIP-FP project "GUARDED". In this three year project we developed a rugged and compact PTR-MS instrument for being used on a robot platform. Starting from the established "Compact PTR-MS" model we performed some preliminary tests in a real-life scenario, i.e. sniffing paper boxes containing explosives, chemical warfare agents, toxic industrial compounds and harmless everyday substances. Based on these results we went on with detailed analysis of the different substances in their pure form in the lab, utilizing all available PTR-MS instruments (PTR-TOF 8000, PTR-TOF 2000, HS PTR-MS, Compact PTR-MS) to gain the highest level of knowledge about the characteristics of the substances. Furthermore we developed a simple form of a pre-concentrator coupled with thermal desorption and integrated it into the final GUARDED prototype. The software interface had to be fundamentally adapted. Starting from the established "PTR-MS Control" software that gives as much information as possible about the measurement process (instrumental parameters, voltages, masses, count-rates, temperatures, etc.) we developed a highly user-friendly and flexible graphical user interface (GUI) for the fully automated instrument. Now the operator does not need specific knowledge about chemistry or physics but sees directly on the display which of the pre-set substances have been detected and at which threat level.

Introduction

The official abstract of the Joint Investment Programme - Force Protection (JIP-FP) "Generic Urban Area Robotized Detection of CBRNE Devices" (GUARDED) according to the website of the European Defence Agency (EDA) [1] reads:

"The aim of this project is to demonstrate a remote controlled mobile platform for sniffing a suspect and/or dangerous area, having on board a set of complementary CBRNE sensors to provide a safe diagnostic obtained through data fusion between various sensors, enabling weddings and solving the old paradox of the need for compromising between resolution and detection. Therefore, after a state of the art of various detection techniques allowing to give an overview of what can be detected and how nowadays, use cases scenarios will be established with the help of operational experts to place the project in a realistic context. From then, an intensive trials campaign will conducted. Technologies like Ground Penetrating Radar techniques for localisation, even through walls or buried objects, Proton transfer Reaction coupled with Mass

Spectrometry, Chemical and Biological based on handheld devices and improving new sampling techniques etc. will be used. To validate the approach, a trial period is planned after the integration & tests phase, which is traditionally crucial, allowing to point out and measure the effects of the project, i.e. completion of the inspection & securing mission."

Already in the first phase of planning it became clear that GPR and IMS are technologies for a quick and approximate estimation whether an illicit substance is present or not. In contrast, PTR-MS can identify and quantify substances at a very high level of accuracy while on the other hand consuming more space and payload on the robot platform. Therefore it was decided that two platforms would be built, one carrying the "exploratory" sensors and one the more exact PTR-MS. In this presentation only the latter one will be presented due to confidentiality issues.

Experimental Methods

The GUARDED PTR-MS prototype was developed in parallel to the PTR-QMS 300, i.e. it is a further development of the former "Compact PTR-MS" and therefore equipped with IONICON's established PTR ion source coupled with a quadrupole mass filter. The vacuum system consists of two turbomolecular and one pre-vacuum membrane pump. The whole system is entirely computer controlled via an embedded PC that is continuously monitoring the system status and providing a high level of safety, e.g. by turning off the voltage supplies in case of a vacuum failure, etc. A second embedded PC with Windows CE as operating system acts as the platform for the installed GUARDED GUI. Additionally this prototype is equipped with a simple form of a pre-concentrator combined with thermal desorption. A high-power fan draws large amounts of (contaminated) air for a pre-defined time through a fine metal mesh. As especially vapors from explosives are known to be very adhesive, the common harmless air compounds will pass through the mesh whereas the explosive vapors will stick to it. After several seconds the fan is turned off and a current running through the mesh is heating it ohmically. The evaporating explosive molecules in their concentrated form are then directly drawn into the PTR drift tube via a heated capillary.

The laptop computer controlling the instrument and displaying the results is connected via common WLAN. In addition the instrument itself is equipped with a touch-screen display that can be used for displaying the measurement results, i.e. alarms, substance identification, etc. Thus, the PTR-MS can be used as a "standalone" instrument, i.e. without the need of an external computer.

The GUARDED prototype is installed in a box with roughly 55 cm side length and the previously mentioned pre-concentrator add-on is mounted on top. The whole system weights around 60 kg. With the aid of exactly dimensioned shock-absorbers the instrument is mounted on the robot platform provided by the project leader ECA (France), together with the battery pack that is needed for cordless operation of the PTR-MS.

Results

In order to gain solid knowledge about the behavior of various groups of dangerous substances (explosives, CWA's, TIC's, etc.), we started by analyzing the compounds in pure form in a lab environment. As this turned out to be a scientifically highly demanding and interesting topic, we decided to go beyond the requirements of the project and extend our investigations by extensive studies of detectability, E/N dependence, comparisons between different instrument types (quadrupole and TOF), etc. These results were published in [2] and [3] (explosives and CWAs) and very recently we additionally investigated illicit and prescribed drugs [4].

Combining all of this knowledge led to a highly sophisticated substance identification software which is shown in Figure 1. Not only does the software monitor the protonated parent ion masses but additionally the isotopes and important key fragments. As the ratios of all these masses are known due to the above-mentioned studies, a specially developed algorithm can distinguish between harmless everyday substances (perfumes, cleaning agents, flavors, etc.) and a dangerous substance at a very high confidence level, even if they share the same nominal mass.

Furthermore the software is extremely flexible, i.e. by knowing the isotope and/or fragment ratios the list of detectable substances can be easily expanded by an operator within minutes. In Figure 1 a set of substances was chosen as an example. Then a vial with strongly diluted chloropicrin (CWA) was placed in front of the PTR-MS inlet and the software identified chloropicrin and immediately raised alarm when the concentration exceeded the preset threshold with a response time of about 1-2 seconds.

In the presentation we will further demonstrate that this instrumental set-up not only works perfectly for a series of other dangerous substances but also that even highly emitting settings like e.g. garbage cans, adulterated milk, nitrobenzene containing soap, etc. do not cause false alarms.

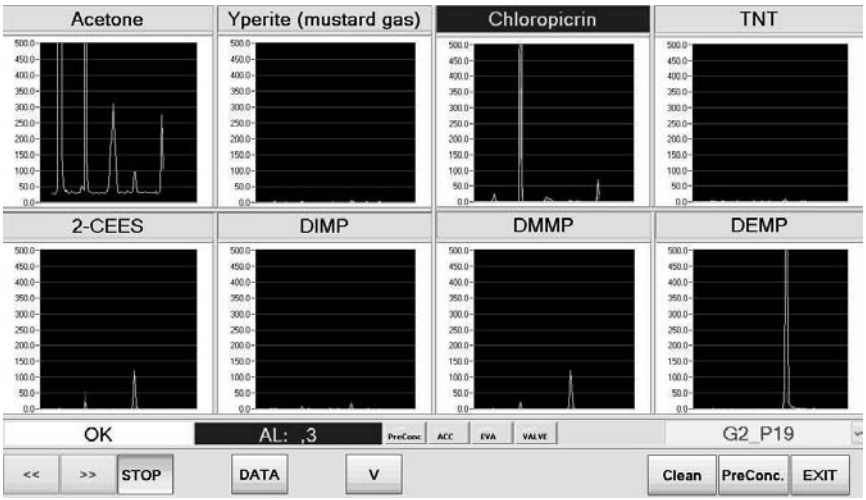

Figure 1: Screenshot of the GUI running on the laptop that is connected to the GUARDED prototype via WLAN while detecting the CWA chloropicrin.

Acknowledgement

Work was supported by the European Defence Agency via a JIP-FP project. CAM wishes to acknowledge the EPSRC (EP/E027571/1) that in part supported this work. FP and SJ acknowledge the support of the Community under a Marie Curie Industry-Academia Partnership and Pathways grant (Grant Agreement Number 218065).

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Contributed Papers (Posters)

Recording of volatile chemicals released by bed bugs during and after blood-feeding and mating by PTR-MS

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Abstract

Semiochemicals released by isolated groups of bed bugs, *Cimex lectularius*, during and after feeding on a human volunteer, were studied by means of combined Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) and video analysis. In this way it was possible to measure semiochemicals released by the animals during specific behavioural activities. The most distinct releases were always observed during or close to the termination of mating attempts, corresponding to the well known defensive sprays that bed bugs release to prevent mating attempts. Bed bugs mate by traumatic insemination, where the male penetrate the female abdomen with his hypodermic genitalia and ejaculates into the female's body cavity. Identification of the released semiochemicals was done by collection of the air samples on adsorption tubes with subsequent analysis by thermal desorption and gas chromatography with mass selective detection. The main components of these releases were always (E)-2-hexenal and (E)-2-octenal, with only minor contributions from other compounds. The two components were observed in ratios mostly between 1:3 and 3:1, respectively. The amount of material released could vary over 1000 fold for either of the two components with up to 10 µg released in a single defensive spray. Males did also produce defensive sprays in case of homosexual mating attempts by other males, and no significant differences were observed in the ratio of the two main components of the defensive sprays, from either males or females. Not all mating attempts resulted in the release of a defensive spray. Besides the defensive sprays, small peaks of acetone were observed correlating closely with faecal deposits. This study has demonstrated that combining PTR-MS with video analysis can provide information about semiochemicals released during specific behavioural activities. However, the approach should be combined with other methods, such as GC-MS, in order to discriminate compounds in more complex mixtures.

Effect of seasonality and short-term light and temperature history on monoterpene emissions from European beech (*Fagus sylvatica* L.)

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Abstract

Branch enclosure measurements of monoterpene emission rates have been performed at different positions in the canopy of a European beech tree in natural environmental conditions. Strong and position-dependent standard emission rate variations were observed in the course of the growth season. By using the obtained dataset and a modified version of the MEGAN algorithm, the response of the emissions to short-term light and temperature history was investigated.

Introduction

Monoterpenes ($C_{10}H_{16}$) are a class of highly reactive non-methane volatile organic compounds (NMVOC) emitted by terrestrial vegetation, with estimated global emission rates between 32 and 127 Tg C yr^{-1} [1]. Because of their impact on the budget of atmospheric oxidants and their role as precursors of secondary organic aerosols, more accurate monoterpene emission rate estimates are clearly required. *Fagus Sylvatica* L. trees (European beech) are known to be high emitters of *de novo* synthesized monoterpenes [2,3,4], which can be described by the light- and temperature dependent emission algorithms that were developed for isoprene [5,6]. Next to the response of BVOC emissions to instantaneous light (PPFD) and leaf temperature, the recently developed MEGAN algorithm [6] also considers the role of other factors such as leaf age (seasonality), soil moisture availability and the average PPFD and leaf temperature over the past 24 hours (short-term history) and over the past 10 days (long-term history). Seasonality of monoterpene emissions from BVOCs was already considered by Holzke et al. to some extent [4], but the results of the present work show that temporal variation of the monoterpene standard emission rate also strongly depends on the position of the leaves in the canopy. The effect of short-term light- and temperature history has already been studied for young Fagus sylvatica L. saplings at controlled growth chamber conditions [7] and this study has now been extended for an adult tree in natural environmental conditions.

Experimental Methods

Monoterpene emissions from four branches at different positions in the canopy of an 85 year old *Fagus sylvatica* L. tree in an experimental forest (Gontrode, Belgium, 50°59'N, 3°47'E) were measured using PFA branch enclosures, which were continuously supplied with dust-, ozone- and VOC-free ambient air (4 L min^{-1}). Two enclosed branches were located in the upper canopy and are designated as the sunlit and semi-shaded branches. The branches in the middle and lower canopy correspond to deep shade conditions. All enclosures were provided with PPFD, leaf and air temperature and relative humidity sensors. Measurements were performed from early May to the end of September 2008, with the exception of the month of July. Part of the BVOC-enriched air leaving the enclosures was pumped through individual, thermally insulated and slightly heated PFA tubes towards a manifold located in a cabin at the bottom of a measurement tower providing access to the branches. In the cabin the enclosure air was analyzed for BVOCs with a hs-PTR-MS instrument and for H_2O and CO_2 exchange with an IRGA. Occasionally, air samples were taken from the enclosures for off-line BVOC analysis with TD-GC-MS. Two empty enclosures were used to determine the background values. The PTR-MS ion signal at m/z 137 was used to quantify monoterpenes and the PTR-MS was calibrated regularly by using a gravimetrically prepared dilute mixture of BVOCs in N_2 (Apel-Riemer Inc., CO, USA). The G97 [5] and MEGAN [6] algorithms were evaluated against the experimentally determined emission rates. In order to decrease the discrepancy between the model estimations and the observations, the original MEGAN model was modified in such a way that the number of hours (n) taken into account in the short-term light- and temperature history terms, the factors describing the importance of past PPFD and temperature conditions (λ_1 and λ_2) and the factor controlling light-saturation of the emissions (λ_3) were treated as variables (in contrast to MEGAN where these values were set to 24, 1, 1 and 1, respectively) and were estimated by minimizing the cost between the modified MEGAN model and the experimental data.

Results and Discussion

Whereas the leaf temperature didn't show much variation, incident PPFD values differed greatly between the four branches, with median noon values ranging from 350 and 40 µmol m^{-2} s^{-1} (for the sunlit and semi-shaded branch, respectively) to below 15 µmol m^{-2} s^{-1} for deep shade conditions. Emissions from the enclosed branches in the middle and lower canopy were most of the time below the detection limit. For both branches in the upper canopy, the highest emissions were obtained in early May, shortly after budbreak. Whereas the Standard Emission Factor (SEF value according to G97) for the sunlit branch already started to decrease drastically at the beginning of the growth season, the one of the semi-shaded branch showed a more constant behavior and a clear decline was not observed until September 9th. These results clearly show that the position of the branches in the canopy, which determines leaf morphology and physiology, has a large influence on monoterpene emission rates.

In agreement with previous studies [7], the observed emissions, corrected for T-dependence (through division by the T-related terms in the G97 and MEGAN algorithms), showed a hysteretic behavior as a function of PPFD, with higher values in the afternoon than in the morning. This points towards a dependence of the emissions on the average PPFD values of the past n hours with $n < 24$.

Diurnally averaged monoterpene emission rates from the semi-shaded branch in early May and in August-September are shown in Figure 1. A clear discrepancy can be noticed between the observations and the calculated emission rates according to the G97 and the MEGAN algorithm. A better agreement was obtained when calculating the emission rates with the modified MEGAN

algorithm. Whereas a single set of values for the added parameters in the modified algorithm was sufficient to considerably improve emission estimates during the period from the end of May to the end of September, a significant improvement of the emission rate estimation for early May required a separate set of optimal values. By further dividing the measurement period into subperiods, and by optimizing the added parameters for each of these subperiods, an attempt was made to investigate the seasonal evolution of the optimal values for these parameters for the sunlit and semi-shaded branch.

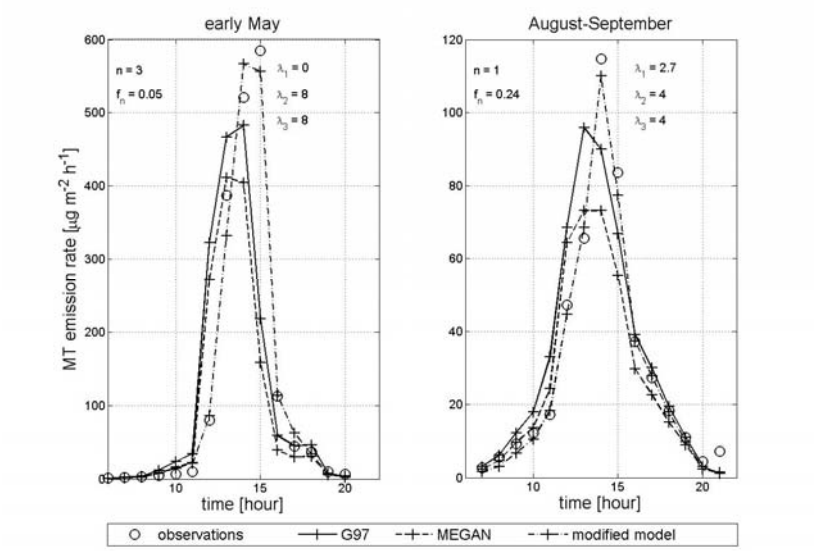

Figure 1: Observed and modeled diurnally averaged monoterpene emission rates for the semi-shaded branch during early May and August-September.

Acknowledgements

The authors wish to acknowledge support from the Belgian Federal Science Policy Office in the framework of the project "Science for a Sustainable Development: Terrestrial Ecology" (IMPECVOC, contract #SD/TE/03B) and the "FWO-Vlaanderen" (contract # G.0031.07).

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Grassland: A source and a sink for biogenic VOCs!

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Abstract

Biogenic volatile organic compounds (BVOCs) play a key in the production of ozone [1] and as precursors for secondary organic aerosol (SOA) formation [2]. Despite the importance of biogenic volatile organic compounds in atmospheric chemistry and physics, there are gaps in the detailed understanding of sources and sinks of BVOCs that hinder more accurate climate modelling and the prediction of reactive carbon budgets.

Over a time period of two subsequent years, fluxes of several BVOCs were measured above intensely managed temperate mountain grassland in Stubai valley, Austria, using a proton-transfer-reaction-mass-spectrometer (PTR-MS). For the measurement of full range mass spectra, a proton-transfer-reaction time-of-flight mass spectrometer was applied additionally to the conventional PTR-MS for several months. VOC fluxes were evaluated using the virtual disjunct eddy covariance (vDEC) method for the PTR-MS data [3], in case of the 10 Hz PTR-TOF data the conventional eddy covariance (EC) method [4] was used.
The most abundant non methane VOC measured above the grassland site was methanol (m/z 33) [5]. It was emitted by the meadow during the entire growing season. Especially the harvesting of the grassland enhanced the emissions of methanol up to one order of magnitude. Continuous emissions of other volatiles than methanol were not detected with the PTR-MS. During a time period after a hailstorm in 2009 however, when the levels of monoterpenes (m/z 137 with PTR-MS and m/z 137.133 with PTR-TOF) as well as other terpenoids (sesquiterpenes, m/z 205.195 and terpenoids, m/z 153.128 with PTR-TOF) in the air were significantly enhanced compared to undisturbed atmospheric levels, deposition fluxes of monoterpenes and other terpenoids to the grassland were detected. In terms of carbon, the monoterpene uptake alone accumulated to significant levels comparable to the methanol carbon emission within the same time period.
This gives rise to the question if deposition processes of non-oxygenated VOCs to the vegetation play a more significant role in atmospheric chemistry than heretofore assumed and if they should be taken into account in the atmospheric VOC budgets.

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The Effect of Milk Storage Conditions on the Volatile Compounds Profile of Trentingrana Cheese: Headspace Analysis by PTR-ToF-MS and GC-MS

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Abstract

PTR-Quad-MS has been successfully used to characterize the volatile organic compounds profile of Trentingrana cheese with the aim of comparing its flavour profile with the one of the most famous Grana Padano and Parmigiano Reggiano [1], to monitor its ripening process [2] and, finally, to correlate the PTR-MS fingerprinting with the odour and flavour profile defined by sensory descriptive methods [3].

In this work we describe one of the first applications of the newly released PTR-ToF-MS instrument [4] to agroindustrial problems and dairy science in particular, focusing on the volatile compounds developed during the long cheese ripening and responsible of the typical odour and flavour of this Parmesan-like cheese [5]. We compared, by means of rapid PTR-ToF-MS profiling, the effects of different procedures for milk storage before cheese making on the quality of Trentingrana: the traditional double milk collection (morning and evening) was compared to a single milk collection. The main goal was to assess if and how the latter more economic procedure affects the final cheese quality and can be used to replace the most expensive traditional approach.

In parallel to the PTR-ToF-MS analysis we performed, on the same samples, head space extraction of volatiles by Solid Phase Micro Extraction followed by Gas Chromatography - Mass Spectrometry detection (SPME-GC-MS) which allows the identification and quantification of several important classes of organic compounds. Principal component analysis on the data GC-MS indicates the presence of differences between the samples, which are related to the milk storage conditions and to the production season. A similar discrimination was obtained by the much faster PTR-ToF-MS analysis. The PTR-ToF-MS fingerprinting coupled with data mining methods can quickly verify that the storage conditions of the milk indeed affect the final quality of cheese. Moreover, these methods highlighted the peaks that play a major role in the classification models: esters for the classification of summer samples and ketones and aldehydes for winter samples [5]. In the case of PTR-ToF-MS the high mass resolution allows in most cases the identification of the sum formula of the selected peaks and s also compound identification.

In conclusion we confirm that PTR–MS is a rapid, non-invasive and effective characterisation tool that provides information, in quantitative and qualitative agreement with GC/MS analysis. Moreover, thanks to the mass resolution (better that 4000) and mass accuracy [6] (better than 5 ppm) of PTR-ToF-MS it was possible to separate compounds containing sulphur or nitrogen atoms permitting their rapid quantification and opening new perspectives for the analysis of important classes of compounds.

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PTR-MS and Chemometrics to Explore the Relationship Between Botrytis Susceptibility and Volatile Profile of Raspberry Varieties

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Introduction

The evaluation of large sample sets is a must in several fields related to life sciences such as genomics and metabolomics which poses a twofold challenge to research laboratories: on one side the necessity to measure in a fast and reliable way (high throughput technologies) and, on the other, the necessity to efficiently extract useful information from the, usually huge, data sets obtained. The complexity of the last problem is further increased in the case of multiclass problems. Here we present a possible strategy to address these issues with large biological data sets, based on chemometrics applied to PTR-MS characterization of raspberry fruits.

Methods

Dataset

The dataset consist of the PTR-MS volatile profiling of 207 raspberry fruits (single berries harvested in 2007) belonging to 13 different varieties (classes) and data on susceptibility to *Botrytis cinerea* evaluated both in field and during storage.

PTR-MS profiling of raspberry fruits was performed according to the procedure previously reported in [1]. *Botrytis* susceptibility was detected by visual inspection of the berries on plants during the harvesting season and on the fruit samples stored at 4 °C for 72 h by trained personnel. Varieties were scored, based on a subjective index of conidia development, in a range from 0, no development of the fungus, to 5, severe damage.

Chemometrics

Principal Component Analysis (PCA) was applied to reduce problem dimensionality and followed by Cluster analysis. Cluster analysis comprises several methods for grouping objects of similar kind into respective categories. Here we applied a Hierarchical Clustering Analysis (HCA) using samples distances as grouping criterion. The HCA basically starts with as many clusters as there are observations. The two closest clusters or observation points are merged, thereafter the two closest clusters or points are merged again and so on until only one cluster remains. The result is usually shown by means of a dendrogram.

To facilitate the identification of the masses responsible for the observed clustering structures and to correlate chemical compounds to *Botrytis* susceptibility, orthogonal PLS (OPLS) was applied on mean centred and Pareto scaled variables. The OPLS method is a recent modification of the PLS method [2], which is designed to handle variation in independent variables (X) that is orthogonal to that of dependent variables (Y). OPLS separates the systematic variation in X into two parts, one that is linearly related (and therefore predictive) to Y and one that is orthogonal to Y. The predictive variation of Y in X is modelled by the predictive components. This partitioning

of the X-data provides improved model interpretability, usually with negligible effect on the predictive power. In fact, OPLS-DA models compress the relevant information for the discrimination, in the case of two classes, to only one predictive component. A simple and effective way to visualize and interpret the data is the use of the so-called S-plot [3]. In this plot, the loading weight w, that in a PLS model expresses the importance of the variable for the model, is plotted against the correlation loading p(corr), corresponding to its reliability. S-plots were used to interpret models in terms of relevant measured variables; only variables having w values considerably different from 0 and significant values of p(corr) were considered important for the models.

Results and discussion

PCA followed by cluster analysis allowed the clustering of the raspberry samples in two main groups. *Botrytis* susceptibility scores are different for the two groups (Fig.1): one group corresponds to fruits with a "low" susceptibility (score < 4) and the other to "high" susceptible fruits (score ≥ 4). In Fig. 1, to simplify the visualization and because indexes for botrytis susceptibility are mean values, PTR-MS data were averaged for each variety as well.

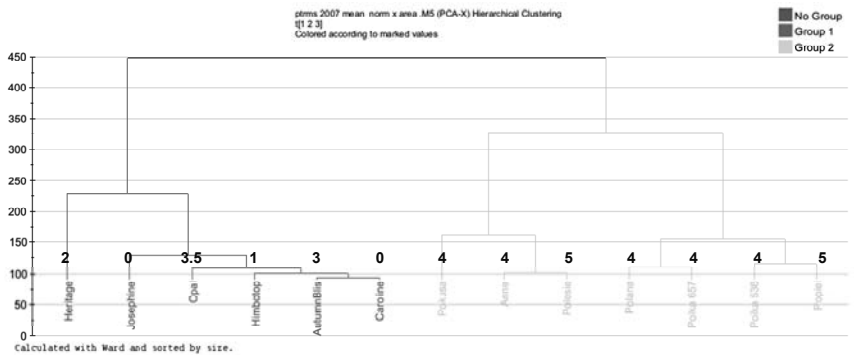

Figure 1: Dendrogram based on PTR-MS volatile profiling of raspberries. Overlapping numbers indicate the level of susceptibility to Botrytis (0 lowest, 5 highest). Green group includes variety highly susceptible to Botrytis cinerea and red group includes varieties with lower susceptibility.

According to the indications of cluster analysis we set a classification model for Botrytis susceptibility by OPLS-DA, which S-plot is shown in fig. 2. The small box of figure 2 indicates the "low" (black points) and "high" (red points) susceptible groups. The most important attributes for the characterization of the "low" group are the signals at m/z 137 and m/z 138. These two masses are most likely associated to protonated monoterpenes (the signal ratio of the two masses corresponds to the ^{13}C natural abundance of a C10 molecule). The results indicate that varieties that are more resistant to *Botrytis* attack emit more terpenes in agreement with GC results on

This work indicate how PTR-MS allows the rapid characterization of large data set and that different chemometric techniques can help the exploration of the obtained dataset allowing the identification of relevant traits and the correlation with independent characterization. In particular the relationship between botrytis resistance and terpene emission can be readily enlightened.

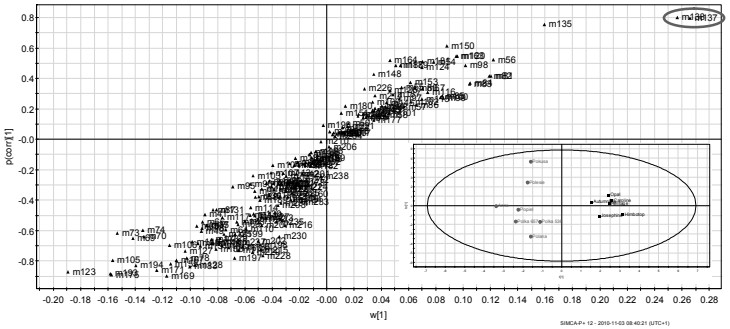

Figure 2: S-Plot from the OPLS classification model (in the small box) for the "low" (black points) and "high" (red points) susceptible groups. The masses highlighted by the red circle are those contributing more to the "low" susceptible group.

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Properly considering PTR-MS drift tube energetic conditions in the determination of PTR rate coefficients

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Abstract

In proton transfer reaction - mass spectrometry (PTR-MS) the availability of reaction rate coefficients between the hydronium ion (H_3O^+) and volatile organic compounds (VOCs) is fundamental for absolute VOC concentration determination from the measured data. Experimental reaction rate coefficient are often affected by large errors and therefore the use of theoretically calculated values is preferred. In principle with PTR-MS, the absolute quantification of VOC concentrations without calibration is possible [1], provided the branching ratios are known. However, for this, the reaction rate coefficients between VOCs and the hydronium ion have also to be known. Several well-established theories may be used to determine ion-neutral molecule reaction rate coefficients. In case of H_3O^+-VOC reactions proceeding in a PTR-MS drift tube, a key factor to be considered is the centre-of-mass energy, which is generally much higher than the thermal energy, due to the additional translational (drift) energy of the ions. Nevertheless, it is common practice to employ collision theories that do not show an explicit dependence on the centre-of-mass energy.

As we discussed in a recent publication [2], the available theoretical results are mostly given for thermal conditions and they should be improved by accurately considering the kinetics of ion-molecule reactions at standard PTR-MS operating conditions. The correction is of much relevance in the case of VOCs having a non-negligible dipole moment. We provide theoretical rate coefficients for a selection of relevant volatile organic compounds in true PTR-MS conditions, see table 1. Reaction rate coefficients between the water cluster of the hydronium ion ($H_3O(H_2O)^+$) and VOCs are also reported. In the calculations we employed quantum chemical results for VOC polarisability and dipole moment extracted from the available literature [2,3]. As mentioned in [2], the parameterization used to calculate the rate coefficients is affected by a maximum error of 5%. Moreover, in the case of sulphur compounds a 3% uncertainty in the quantum chemical results for both the polarisability and the dipole moment further increases the error on the rate coefficients by about 1-2%. For the other selected VOCs the reported 30% error [3] in the determination of the polarisability and dipole moment leads to about a 15% uncertainty in the determination of the rate coefficients. Depending on the experimental set-ups, the drift tube temperature and the primary ion velocity may differ from the standard values considered here. However, at a drift tube temperature of 380 K variations by about 10 K do not significantly affect the reaction rate coefficients. Moreover it can be shown that a 5% increase or decrease from 930 m/s of the ion drift velocity leads to approximately a 1% change in the rate coefficient.

Conclusions

PTR-MS can provide accurate absolute VOC concentrations provided that branching ratios and rate coefficients are known. In general theoretical estimation of reaction rate coefficients are considered more accurate that measured values. The common practice to use literature values of the latter parameters at room temperature is, at least, questionable. For molecules with a low dipole moment the difference with room temperature data is small, but the effect cannot be neglected in general. Indeed it leads to an underestimation of rate coefficients by up to 20% for the VOCs we considered. We suggest to use reaction rate coefficients corrected for this effect in PTR-MS applications.

Table 1: Proton transfer reaction rate coefficients between the hydronium ion (H_3O^+) and selected VOCs at standard PTR-MS working conditions. Reaction rate coefficients between the water cluster of the hydronium ion ($H_3O(H_2O)^+$) and VOCs are also reported. A more comprehensive list will be published elsewhere.

		H_3O^+ k [$10^{-9}cm^3/s$]	$H_3O(H_2O)^+$ k [$10^{-9}cm^3/s$]
Acetaldehyde	C_2H_4O	2,87	2,43
Acetic acid	$C_2H_4O_2$	2,04	1,70
Ethanol	C_2H_6O	2,06	1,76
Acetone	C_3H_6O	2,68	2,21
Pentanal	$C_5H_{10}O$	2,95	2,39
Benzoic acid	$C_7H_6O_2$	2,60	2,04
Benzaldehyde	C_7H_6O	3,62	2,88
Benzene	C_6H_6	1,97	1,53
Toluene	C_7H_8	2,13	1,64
Isopropylbenzene	C_9H_{12}	2,44	1,87
Acetonitrile	C_2H_3N	3,74	3,23
Dimethyl sulphide	C_2H_6S	2,19	1,85
Ethylmethyl sulphide	C_3H_8S	2,26	1,85
Diethyl sulphide	$C_4H_{10}S$	2,36	1,89
Allylmethyl sulphide	C_4H_8S	2,34	1,88
Dimethyl disulphide	$C_2H_6S_2$	2,54	2,07
Diethyl disulphide	$C_4H_{10}S_2$	2,34	2,20
Dipropyl disulphide	$C_6H_{14}S_2$	2,93	2,27

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Correcting the dead time effect in PTR-TOF-MS

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Abstract

Proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) allows for very fast simultaneous monitoring of volatile organic compounds (VOCs) in complex environments. In several applications, food science and food technology in particular, mass peaks with very different intensities can be present in a single spectrum. For VOCs, the concentrations range from the sub-ppt all the way up to the ppm level. Thus, a large dynamic range is necessary. A major factor affecting the linearity in TOF based systems is the detector dead time [1]. In fact, any ion counter is able to discriminate only events which are separated by a minimum time lag, during which the counter is inactive. Events occurring within this dead time are irrevocably lost. Therefore, high intensity peaks in a mass spectrum are a problem because for them the linear dependency of the detector signal on VOC concentration is distorted because of dead time losses. Usually, raw data can be used directly without corrections with an intensity of up to about 0.1 ion/pulse, the Poisson correction allows to correct mass peaks with intensities up to a few ions/pulse.

However, to the best of our knowledge, no reliable and straightforward correction method has been presented in the literature for higher rates. As suggested by Coates [2], limitations are mainly due to an increase of the apparent noise with the detection rate and the actual upper limit depends on the relationship between the dead time and the pulse time and on the probability distribution function of ion arrivals. Here we will discuss a correction method that we recently proposed and that further extends the linear range by at least one order of magnitude [3]. This method does neither rely on any simulations of the instrumental conditions nor on the knowledge of any experimental parameters.

Figure 1 depicts the comparison between ion intensities determined by our method and those estimated using correction methods based on Poisson statistics. The raw signal intensity is also shown clearly demonstrating the effect of the dead time on the peak intensity, i.e. a clear deviation from linearity. The count losses caused by the dead time gap allow at most a few ions to be detected during the same cycle and appear as a so called saturation of the detector. The results for the signal corrected with the Poisson correction are also shown in the same figure. For peak intensities smaller than ~5 ions/pulse, the correction enables to retrieve the correct intensity, while at higher count rates the estimation starts deviating from the correct values. Our method instead allows retrieving the correct count rate even in case of higher ion intensity, thus extending the dynamic range. The point that is off at 90-100 ions/pulse rates is probably related to instrument instabilities that induce a further distortion of signal beyond that caused by the detector dead time. Although our work originated from the necessity of extending the dynamic range of PTR-TOF-

MS instruments in agro-industrial applications, it is by no means limited to this area, and can be implemented wherever dead time corrections are an issue.

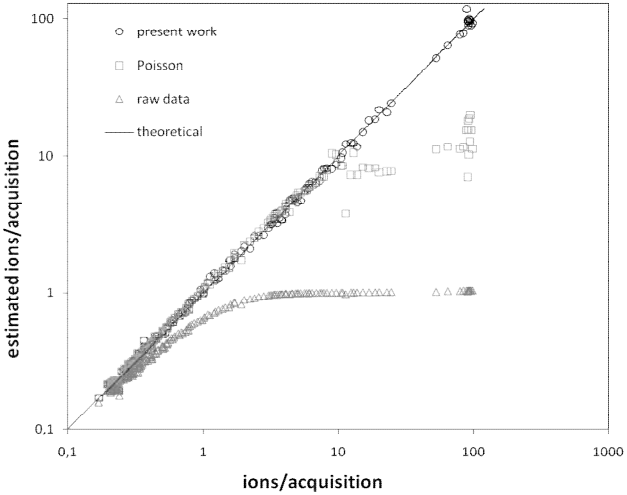

Figure 1: Experimental data. Triangles: distorted signal intensities. Squares: intensity of the signals corrected using Poisson statistics.. Circles: intensities estimated using the present method [3].

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Stress-driven sesquiterpene emissions by transgenic tobacco plants and their link to new aerosol particle formation

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Abstract

New particle formation is ubiquitous in the atmosphere. It is highly relevant for humans and climate because of its effects on health, radiation balance and due to the possible contribution of newly formed particles to cloud condensation nuclei. However, the formation process is currently not well understood. Especially the biogenic contribution and the stage at which they contribute, is highly discussed. We are investigating this phenomenon with field campaigns, smog chamber studies and with greenhouse experiments. The purpose of this paper is to emphasize the role of biogenic alkenes such as terpenes, in new aerosol particle formation. We present some results of our greenhouse experiments, in which sesquiterpene emissions were well correlated with the observed particle formation and clearly showed an ozone stress derived emission.

Introduction

Atmospheric new particle formation is a common phenomenon occurring nearly everywhere at the Earth's surface as well as above [1]. These newly formed particles may affect cloud formation, heterogeneous processes and health. It is known that a large portion of ambient fine particulate matter is organic aerosol from secondary processes [2]. A new climate feedback process linking increased hydrocarbon emissions and aerosol production to climate change issues is under discussion. For each of the processes knowledge on the chemical composition and the controlling parameters for nucleation are essential [3].

Terpenoids encompass several wide classes of compounds, including monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), diterpenes and larger oxygenated terpenes (e.g., $C_{10}H_{18}O$). These compounds are emitted from coniferous (evergreen) as well as broad-leaved trees as a function of temperature, or both temperature and light [4]. They react with OH, O_3, and NO_3, the common atmospheric oxidants, with lifetimes that range from minutes to days [5].

It is known that the total organic carbon can comprise 25– 65% of the fine aerosol (diameter <2.5μm) mass in some regions [6] and that the emission by vegetation of volatile organic compounds (VOC) is approximately 1150 C Tg per year [7,8]. However, the exact understanding of the pathways from emission of VOCs to the particulate phase still includes far too many unknowns and fragile products not yet investigated to draw final conclusions. According to a recent proposed theory ozonolysis products of sesquiterpenes, react to produce low-volatility organic sulfates or secondary ozonides [9].

The necessity to further investigate the key role of biogenic VOC emissions is essential as it links the anthropogenically forced climate change to biosphere feedback processes. In our studies we

aim to find a link, between the stress induced emissions from biosphere and the newly formed aerosol particles that are observed mainly above coniferous forests

Experimental Methods

To gain a high time resolution of in our case, interesting volatile organic compounds (VOCs) we applied a high sensitivity PTRMS from Ionicon. E/N ratio is adjusted at 117Td [10] and calibrations are performed before every measuring period. In every case study particle number is recorded by an ultrafine Condensation Particle Counter (TSI, model 3025a), ozone concentrations are monitored by an ozone analyzer (model APOA-350E, Horiba) and NO concentrations are monitored by a NO-NO_2-NO_x chemiluminescence analyzer (Model 42S, Thermo Environmental Instruments).

Greenhouse experiments

The presented preliminary experiments have been conducted in our greenhouse facilities, at Goethe University, Frankfurt. Tobacco plants have been genetically modified by the MPI Jena in order to emit large sesquiterpene (SQT; $C_{15}H_{24}$) amounts, here farnesene. Using modified and wild type tobacco plants for intercomparison the role of ozone in new aerosol particle formation has been investigated. Here, we present our first greenhouse demonstration of aerosol nucleation from oxidation of volatile organic species emitted by living plants.

Results

The presented results are connected with the performed greenhouse experiments. Treated tobacco plants, induced the production of sesquiterpenes (mainly farnesene). From our measurements it looks like farnesene and ozone form new particles in the presence of moderate water vapor (RH = ca. 40 %, T = ca. 30°C, H_2O mixing ratio = ca. 9 ppthv), with a nucleation rate between 9 and 50 particles·ccm^{-1} · sec-1 at 3 nm in diameter. Using a condensation sink of between $2x10^{-3}$ and 0.01 per second, leads to a lifetime of new particles, until their collision with larger particles and their potential removal (uptake) by larger ones, of about 100-500 s. This gives 20.000 to 30.000 particles per ccm as observed when considering a sesquiterpene mixing ratio of 100 ppt in the presence of 2 ppb of NO and 40ppb of ozone.

A distinct daily pattern through a week of experiments is shown at *figure 1*. A good correlation between the number of particles above 3nm in diameter and the estimated volume mixing ratio of farnesene, is applicable.

During the last day of the experiments, the plants were further treated with methyl jasmonate, to increase farnesene emissions. Enclosing single plants in a Teflon foil and inserting an enlighted ozone lamp for several minutes resulted in a rapid increase of particle number concentration leading to an increase beyond the upper detection limit of 100.000 particles/cm^3. This behavior was similar for both wild and transgenic type, but we observed differences in the measured ozone levels. Ozone concentrations reached 1ppm at the genetically modified plant, while at the wild plant ozone raise only up to 290ppb, suggesting a stronger defensive mechanism.

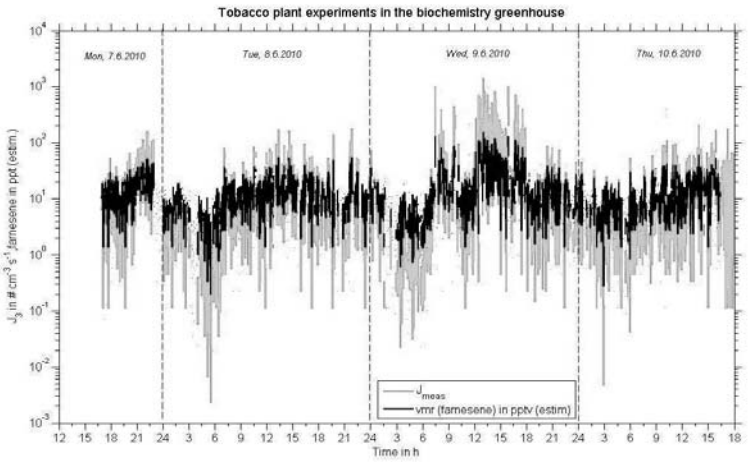

Figure 1: Timeline of farnesene enclosure concentration (in ppt) matching the measured J_3 (in particles·cm^{-3}·s^{-1}).

Discussion

During our greenhouse experiments it became apparent that in presence of sesquiterpene-emitting plants, ozone catalyzes particle formation. We would have predicted that the sesquiterpene-emitting plants have greater ability to buffer ozone. On the contrary, the sesquiterpene-emitter was inferior to the wild type in its ability to combat rising ozone levels. Perhaps tobacco has some unknown but highly reactive terpene that is an efficient ozone scavenger. We were intrigued by the results and we will try to replicate them, with transgenic tobacco and corn plants that emit large and different types of sesquiterpenes. It looks like that the production of these terpenes, appears to take place in order to protect the plants from the deleterious effects of ozone, suggesting that the reactivity of ozone with the emitted sesquiterpenes is biologically relevant and contributes to new aerosol particle formation.

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Differences of Volatile Organic Compound (VOC) contents in traditional and modern apple varieties measured by Proton Transfer Reaction–Mass Spectrometry (PTR-MS)

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Abstract

Chemodiversity of apples regarding aroma is an active research field, allowing to relate sensory perception, quality, and the influence of cultural measures before, at and after harvest to chemical odor components. The aim of the present study is the characterization of volatile organic compounds (VOCs) emitted by apples using proton transfer reaction-mass spectrometry (PTR-MS) in order to discriminate between traditional and modern apple varieties at harvest, after defined storage times and in different harvest years.

Introduction

With around 10% of the EU-27 production, South Tyrol is one of the most important apple growing areas in Europe. Golden Delicious is still the leading variety with 43% of total production, followed by Gala with 16%. The remaining varieties (Granny Smith, Red Delicious, Braeburn, Fuji and Pink Lady®) do not exceed 10% each [1]. Another aspect worth mentioning is that most of all modern varieties in the Western World have a similar genetic background [2], causing a restricted spectrum in agricultural biodiversity. In the entire world, there are more than 7000 apple varieties, characterized by various organoleptic properties and aromas [3].

Volatile organic compounds (VOCs) play an important role in the study of the properties of apple varieties. They are fundamental metabolites that can be used to study their chemodiversity. VOCs are directly connected to the perceived sensory quality of fruit and provide fast, non-invasive means for analysing metabolites and physiological aspects [4].

Experimental Methods

This study included 35 traditional local varieties from the germplasm collection of Laimburg Research Centre in South Tyrol (Italy). In addition, the seven principal varieties commercially grown in South Tyrol were analysed. Ten apples for each variety were measured in 1 L PFA jars with minimal VOC emission (AHF, Tübingen, DE) at 20°C under a water-saturated stream of N_2 (250 mL min^{-1}): Empty jars were flushed for 10 min with water-saturated N_2 for background measurement, the jar was charged with one apple, and data was acquired after 3 scans of equilibration time. Two different storage time points were analysed: i) immediately after harvest and ii) after a storage period of 60±10 days (2°C, 90% air humidity), followed by 3 days of shelf-life at room temperature.

The PTR-MS instrument was operated at standard measurement conditions: mass scan: *m/z* 21-210, dwell time: 500 ms, data acquisition: 6 scans, drift tube voltage: 600 V, drift tube pressure: 2.00 ± 0.05 mbar, O_2^+/ H_3O^+ ratio ≤ 0.1 %.

Results and discussion

Due to the great diversity of molecules in the apple's headspace, causing a high number of signals measured by PTR-MS, the raw data set was subjected to Principal Component Analysis (PCA) in order to find the most important masses that best represent the variance of the system. The first PC (49.4% of the total variance) was mainly related to fragments or signals of terpenes (mostly monoterpenes and sesquiterpenes) or terpene-related metabolites. Mass *m/z* 81, which has been interpreted as a common terpene fragment[5] and is typically the most abundant peak in PTR-MS spectra of commercial terpene standards, had a great variance in the head-space analysis of the apple varieties of this study. The presence of terpenes, one of the most abundant being α-farnesene, in apple aroma is in accordance with literature [6]. The high abundance of this signal might be due to the high volatility and low water solubility of terpenes, the great variance of these compounds across the analysed varieties due to genetic differences in terpene biosynthesis.

Esters, alcohols, ketones and aldehydes contributed most to the second PC (14.9% of the total variance). The lower contribution of these compounds to the total variance of the system compared to terpenes can be explained by their higher water solubility [7].

Great differences were observed in the PCAs between fruits analysed immediately after harvest and after the storage period. This may be due to the fact that during the storage and shelf-life period the different varieties ripened and developed their "individual" flavours, giving rise to fingerprint mass spectra for every single variety. The most important changes occurred in the second PCs because they are functionally related to natural ripening and senescence processes of apples [8]. Accordingly, they are expected to change significantly during the storage and shelf-life period.

Conclusions

In this study PTR-MS was used to monitor the chemodiversity of VOCs in the headspace of modern and traditional apple varieties. The method's obvious strength is a fast and simple measurement procedure. Our data analysis confirmed a widespread chemodiversity of apple aromas. VOCs emitted by modern varieties turned out to be more closely related, in line with limited genetic variation between them. Moreover, the aromatic fingerprint analyses are generally reproducible between different harvest years if the same sampling and measuring conditions are maintained. In conclusion, our results open the possibility of using PTR-MS as a valuable tool for quality control, production monitoring, and improving appreciation for the traditional biodiversity of apples.

Acknowledgements

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The dynamics of aroma release during the consumption of candies with different structures. Relationship with temporal perception

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Abstract

This study aims at investigating the role of candy texture on the dynamics of aroma release. The main originality was to simultaneously apply dynamic instrumental and sensory methods. Four candy textures were established by varying gelatine content between 0 and 15% w/w. They were flavoured with 3 aroma compounds having different physicochemical properties and different sensory attributes. The highest *in vivo* release, monitored using Proton Transfer Reaction Mass Spectrometry with a trained panel, was obtained for the 2%-gelatine sample for all aroma compounds. The dynamics of aroma and taste perception were characterized using the Temporal Dominance of Sensations (TDS). The dominant sensation for the liquid product was the "strawberry" note. For other products, the temporal characteristics of perceptions were more complex. The global duration of the dominance period (all sensory attributes taken together) increased linearly with gelatine content. Data highlighted that aroma release resulted from interaction between product properties and oral behaviour. Some relations with the dynamics of perception have been established, essentially between temporal parameters.

Introduction

The effects of product structure on aroma release result from the combination of physicochemical (entrapment of aroma compound in product structure and/or obstruction to their mass transport) and physiological phenomena (modification of oral behaviour) [1]. Most of the time, increasing product viscosity or firmness results in decreasing aroma release and perception, even if some contradictory results exist. A better understanding of relationships that can exist between sensory perceptions and physicochemical properties of foods has always been a tempting objective to better control food organoleptic properties. In literature, only a few studies focused on perception over time by applying the Time-Intensity sensory method and proposed some relations with the dynamics of *in vivo* aroma release.

The objective of the present study was to evaluate the impact of candy structure on the dynamics of *in vivo* aroma release and to propose some relationship with temporal sensory perception (method of Temporal Dominance of Sensation, TDS). The use of instrumental and sensory methods in parallel constitutes an original approach to better understand aroma release and perception and to identify some relationships between these two phenomena.

Experimental Methods

Products

Four candies with different structures were prepared by modifying their gelatine content (0%, 2%, 5% and 15% v/v). The concentration of other constituents remained constant (glucose syrup: 25%; sucrose: 25%; citric acid: 1%; red dye: 0.25%). Products were flavoured with 0.4% of the concentrated aroma solution (diacetyl, ethyl hexanoate, *(Z)*-hex-3-en-1-ol).

PTR-MS measurements

In vivo aroma release kinetics were measured using a High-Sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS) (Ionicon Analytik, Innsbruck, Austria). The PTR-MS instrument drift tube was thermally controlled (60°C) and operated with a voltage set at 600.1 (±0.4)V. Measurements were performed using the Multiple Ion Detection mode on *m/z* 83 (Z-3-hexen-1-ol), *m/z* 87 (diacetyl) and *m/z* 145 (ethyl hexanoate) with a dwell time per mass of 0.1 s.

Measurements of *in vivo* aroma compound release kinetics

Twelve panellists (4 men / 8 women, 22-45 years old) were specifically trained to perform sensory analyses in parallel to *in vivo* measurements. Nose space air was sampled *via* two inlets of a stainless nosepiece placed in both nostrils of the assessors. The inlet of the PTR-MS instrument was connected to the sampling device *via* a 1/16" PEEK™ tube maintained at 60°C. The air room was first analyzed during 10 s. Then, after positioning the sampling device in the two nostrils, panellist breath was analyzed for 30 s. For liquid product, panellists were asked to sip 20 mL of product from a straw and to consume it as they did normally. For gelled samples, panellists put 4 g in mouth and let them melt. The time of the first swallowing was noticed. More details concerning the protocol are described in Déléris et al. 2010 [2]. Maximal intensities I_{max}, times t_{max} at which I_{max} occurred and areas under the curve AUC were extracted from each individual release curve for both the oral phase of consumption (phase 1) and the phase after swallowing (phase 2).

Sensory analysis

Sensory analysis was performed simultaneously with nose-space measurements using the method of Temporal Dominance of Sensations (Saint Eve*, et al.*, 2010). Six aroma and taste attributes were selected: sweet, sour, strawberry, peach, green grass and butter. During product tasting, subjects had to choose the dominant attribute in the list at a given time and were free to select an attribute several times. Data were collected on a computer screen with FIZZ software.

Statistical Analysis

Statistical analysis of variance and Student's t-test were carried out on *in vivo* release data, using the GLM (general linear model) module and the t-test module of the SAS® software package. A Student-Newman-Keuls (SNK) full comparison test was also carried out to screen for significant differences between individual instances of sample type. The level of significance was established at $p<0.05$.

For TDS data, dominant rates were calculated by attribute for each product and each time. Data interpretation was performed in regards with "the chance level" (dominance rate that can be reached by chance for one attribute) and "the significance level" (the minimum value that must be reached to consider the dominant rate as significantly higher than the "chance level").

Results

Release kinetics were rather similar for all ions, with a slight increase in released amount between products with 0% and 2% of gelatine, a similar shape for release kinetics for products with 2% and 5% of gelatine and a clear decrease in the released amount for the 15% gelatine product (figure 1). The initial release rate was also impacted, decreasing when gelatine content increased.

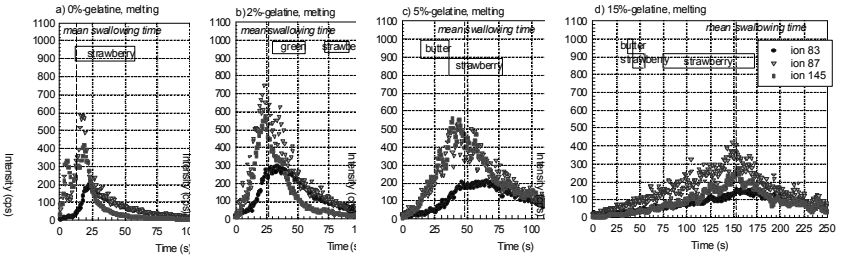

*Figure 1: Mean release of ion 83 ((*Z*)-hex-3-en-1-ol), ion 87 (diacetyl) and ion 145 (ethyl hexanoate) obtained by* in vivo *measurements with PTR-MS and mean duration of the dominant perception measured with the DTS method (boxes) during the consumption candies. The vertical dashed line indicated the mean time at which the first swallowing occurred.*

Before the first swallowing event, for ions *m/z* 83 (*(Z)*-hex-3-en-1-ol) and 87 (diacetyl), the 2%, 5% and 15% gelatine samples had the most intense release (I_{max1}) whereas only the 15% gelatine product released the highest amount (AUC_1) of aroma compounds. Concerning ion *m/z* 145 (ethyl hexanoate), no significant difference between products was noticed on I_{max1} parameter and both 5% and 15% gelatine samples released a higher amount of aroma compound (higher AUC_1) than the 2 others products. After the first swallowing event, the shape of aroma release kinetics remained similar, with a more intense and more important release of aroma compounds from products with 2 and 5% gelatine than with 0 or 15% gelatine for the three ions. The signal durations for ions *m/z* 83 (*(Z)*-hex-3-en-1-ol) and *m/z* 87 (diacetyl) were similar for 0%, 2% and 5% gelatine products but increased (1.7-fold and 1.4-fold factors respectively) for 15% gelatine product. Concerning ion *m/z* 145 (ethyl hexanoate), products with 0 and 2% gelatine were the least persistent.

Concerning sensory results, the global duration of the dominance period (all sensory attributes taken together) increased linearly with gelatine content, varying from 43 s for 0% gelatine sample to 140 s for the 15% gelatine sample. The dominant sensation for the liquid product was the "strawberry" note. For other products, the temporal characteristics of perceptions were more complex: the "strawberry" note was also evaluated as dominant at some consumption times but was preceded by the "green" note for the 2% gelatine sample or by the "butter" note for the 5% gelatine and the 15% gelatine samples.

Discussion

From all these results, the main role of product structure was highlighted. Before the first swallowing, the amount of aroma release was higher for 15% gelatine product than for other

products for all the 3 ions, probably because of a much longer residence time for the product with the longest melting time. The aroma release was more intense for products with intermediate gelatine contents (2 and 5% gelatine): even if the residence times in mouth of these products were shorter than for the 15% gelatine product, aroma compounds were probably more easily and more rapidly released from these less strong gels. For the liquid sample, the combination of a short residence time in mouth and a limited retention of aroma compound (no three-dimensional network) induced the fastest release. After the first swallowing, aroma release appeared to be less intense for 0% and 15% gelatine products than for the 2 others, probably in relation with product structure. The liquid nature of the 0% gelatine sample can induce a lowest thickness of product deposit in the pharynx cavity is, leading to lowest aroma release. For the 15%-gelatine product, the long residence time in mouth before swallowing probably implied a higher amount of aroma release during this period and thus limited the amount of aroma compound available for release after swallowing, in spite of a thickest deposit on mucosa.

We assumed that the most pertinent parameters to compare both data sets were the dominance duration and the sequences of sensory attributes for sensory parameters and the t_{max} value for each ion and the comparison between signal levels (intensity ratio) between each ion for instrumental data. Mean sensory dominances were represented together with mean release kinetics for each product on Figure 1. For the 0% gelatine sample, the “strawberry” attribute was the only one mentioned, probably because of the early release of the related aroma compound (ethyl hexanoate, *m/z* 145) and the very short residence time of product in mouth, not sufficient for the perception of other attributes. It is also interesting to notice that “strawberry” perception perfectly coincided with swallowing. When gelatine content increased, perception became more complex and occurred more and more early before swallowing, such as aroma release. In the case of the 2% gelatine sample, the apparition of the “green” attribute during 17s just after swallowing can be directly related to the release of *m/z* 83 ((Z)-hex-3-en-1-ol), which was more important from this product than from the 3 others (highest $Imax_2$ and AUC_2). For the 5% and 15% gelatine samples, the “green” note was no more perceived as dominant, probably because of a lowest release amount of *m/z* 83 but also an increase in the released amount of *m/z* 87 (diacetyl) responsible for “butter” note, favoured by an increase in residence time in mouth.

From these results, some links could be established between sensory and release data, essentially concerning the temporal parameters. But conclusions were mainly based on a descriptive data analysis and the variety and the complexity of involved phenomena made difficult the establishment of clear quantitatively relationships between both sets of data.

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Influence of composition (CO2 and sugar) on aroma release and perception of mint-flavored carbonated beverages

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Abstract

The aim of the present work was to identify and quantify physical mechanisms responsible for in nose aroma release during the consumption of mint-flavoured carbonated beverages in order to better understand how they are perceived. The effects of two composition factors (sugar and CO_2) were investigated on both the sensory and physicochemical properties of drinks by studying *in vitro* and *in vivo* aroma release. Sensory results revealed that the presence of CO_2 increased aroma perception regardless of the sugar content. In agreement with volatility parameters, *in vivo* measurements showed that carbonated drinks released a greater quantity of aroma compounds in the nose space than non-carbonated ones. CO_2 seemed thus to induce large modifications of the physicochemical mechanisms responsible for the aroma release and flavour perception of soft drinks. Moreover, sugar content seemed to have an impact (increase) on aroma perception only in the case of non-carbonated beverages. Sensory interactions were thus observed, in particular, between sweet and aroma perceptions. For carbonated beverages, sugar content had an impact only on aroma release, but not on their perception.

Introduction

The main sensory properties of soft drinks induced by carbonation are sparkle and effervescence and are responsible for flavour enhancement and refreshing sensation. These properties largely contribute to consumer choices and preferences. A better understanding of the phenomena involved represents thus a real challenge for the food industry.

The presence of carbon dioxide in beverages can modify their taste and flavour perception [1].

The present study aims at identifying and quantifying the mechanisms of aroma release from flavoured carbonated beverages in oral and nasal cavities during consumption that are responsible for their perceptions. The original aspect of this study is the use of an integrated approach combining physicochemical and sensory methodologies to investigate the effects of sucrose and CO_2 (the major constituents of carbonated soft drinks).

Experimental Methods

Products

Four flavoured beverages varying in the presence or not of sucrose (1%w/w) and carbon dioxide (5 g/L) (CO_2). The beverage products were flavoured to 0.1% (w/w) with a mint flavour containing three aroma compounds mixed with propylene glycol (Z-Hex-3-en-1-ol, menthol, and menthone) [2].

Characterization of *in vitro* and *in vivo* aroma release by PTR-MS.

The influence of beverage composition on the dynamic release of aroma compounds was studied using a proton transfer reaction mass spectrometer (*in vitro* and *in vivo* online measurements). The PTR-MS inlet was connected to samples via a 1/16 in PEEK tube maintained at 60°C. The PTR-MS instrument drift tube was thermally controlled (T_{drift}=60°C) and operated at P_{drift}=200 Pa with a voltage set of U_{drift} = 600 V. Measurements were performed with the multiple ion detection mode on 13 specific masses with a dwell time of 0.1 s per mass.

For *in vitro* measurements, an aliquot of 20 mL of beverage was poured into 100 mL glass vials. Vials were hermetically sealed and stored for 24 h at 10 or 25°C before analysis. The headspace mixture was continuously extracted for 10 min with a constant air flow (from 10 to 30 mL/min depending on the experiment). Areas under curve (AUC) were extracted from release curves and investigated by a one-way analysis of variance (product) for each ion to compare products.

Four panellists were recruited for *in vivo* measurements. During a session, subjects drank eight beverage samples at 10°C according to a defined procedure, in order to reduce the inter individual variability: after positioning a homemade nosepiece in the two nostrils, panelists were asked to breathe regularly for 30 s. Fifteen milliliters of beverage was then sipped with a straw. Panelists had to keep the beverage in their mouths for 6 s. At the end of this 6 s period, they were asked to swallow as they did normally, mouth closed, and to breathe into the nosepiece [2].

Sensory Procedure.

The discontinuous dynamic sensory procedure, which permits one global attribute to be monitored several times during the consumption of a single sample, appeared to be the most appropriate methodology. During the nose-space measurement of aroma release, subjects scored the perceived overall aroma intensity at three main consumption times: (i) upon introduction of the beverage into the mouth; (ii) when swallowing (6 s after introduction of sample into the mouth); and (iii) 60 s after introduction of the beverage into the mouth (persistence). For each sample, a 10 cm unstructured scale anchored with the terms “not intense” and “very intense” was used [3].

Statistical Analysis.

Statistical analysis of variance (ANOVA) and Student’s t test were carried out on physicochemical and sensory data, using the GLM (general linear model) procedure and the t test module of the SAS software package. A Student-Newman-Keuls (SNK) full comparison test was also carried out to screen for significant differences between individual instances of sample type and timing.

Results

The presence of CO_2 in beverages significantly increased gas to product partition coefficients, regardless of the aroma compound or temperature considered [2]. For both temperatures, this

effect was much more pronounced for (Z)-hex-3-en-1-ol (5-9 fold increases) than for menthol and menthone (1.5-2.5 and 1.5-fold increases, respectively), independent of the presence of sucrose. Concerning the effect of sucrose on gas-to-product partition coefficients, results were similar regardless of the temperature ($p<0.05$); sucrose addition only increased the volatilities of menthol and menthone in carbonated beverages (1.1-fold increase), and this effect was not preponderant in comparison with the effect of CO_2 addition.

Concerning the effect of product composition, CO_2 addition seemed to have a preponderant effect with regard to sucrose addition on in-nose aroma release after swallowing: the carbonated beverages had significantly ($p<0.05$) higher values for AUC_2 than the non-carbonated beverages for the three ions (ions with m/z 83, 139, and 155) (Figure 1). A 1.4-1.5 fold increase in the AUC_2 parameter was observed for beverages with CO_2 compared to beverages without CO_2. This increase in the quantity of aroma compound released in the nasal cavity when CO_2 was added occurred regardless of the sugar content considered. Sucrose addition tended only to increase *in vivo* aroma release for the three ions for carbonated and non-carbonated beverages, but results were not significant ($p<0.1$).

With regard to the effect of CO_2 addition on aroma perception at introduction into the mouth and at swallowing, a higher intensity for the carbonated beverages was observed compared to the non-carbonated beverages ($p<0.05$). The aroma intensity was increased 1.4-fold for beverages without sucrose and 1.7-fold for beverages with sucrose. At persistence time, a significant effect of CO_2 addition on overall mint aroma intensity was observed only for beverages with sucrose ($p<0.05$). Moreover, sucrose had an impact on aroma perception only during consumption for non-carbonated beverages. A 1.2-fold increase at swallowing and a 1.3-fold increase at persistence in aroma perception were observed when sucrose was added to non-carbonated beverages.

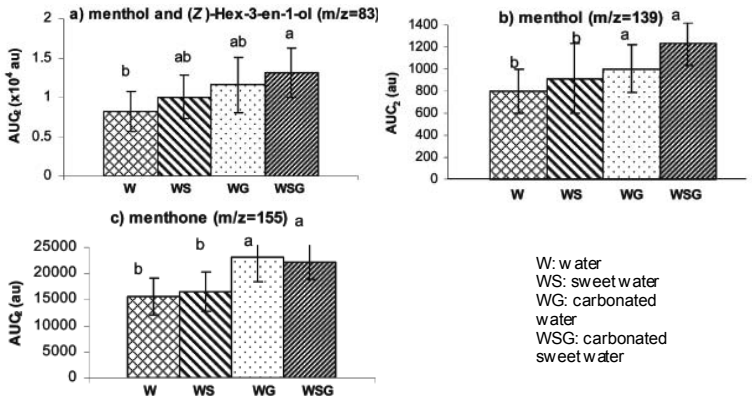

Figure 1: Significant effect of CO_2 and sucrose on the area under the curve after swallowing (AUC_2) (mean value across subjects and standard deviations) for the three ions and the four beverages (ANOVA). Letters a and b indicate means that significantly differ at $p < 0.05$ (SNK test).

Discussion

When the beverage was in the mouth, the presence of CO_2 had no effect on the amount of aroma available in the nasal cavities of the subjects. However, these *in vivo* results were not in agreement with *in vitro* measurements and with aroma perception when the beverage was in the mouth (higher gas-to-product partition coefficient and higher aroma perception for carbonated beverages than for non-carbonated beverages). Several assumptions can be proposed. Differences in volatility properties of aroma compounds between beverages were not sufficient to induce significant differences in aroma quantity in the nasal cavity. Carbonated beverages are more complex products than non-carbonated beverages. It is also possible that when products were in mouth, panellists might report these more complex sensations on the aroma perception scale (higher aroma perception when the drink was in the mouth). Moreover, it is well-known that in the mouth, CO_2 is converted into HCO_3^- at a very high rate by anhydrase carbonic activity: a possible interaction of this phenomenon with the release and sensory perception of flavor in carbonated beverages cannot be ignored.

The presence of sugar had an effect on the aroma perception of non-carbonated beverages, but no physicochemical mechanism was revealed that could explain this phenomenon. To explain perception, sensory interactions between sugar and mint aroma may occur in the absence of CO_2. A congruence phenomenon could be presumed.

Concerning sugar effect in the case of carbonated beverages, results highlighted that sugar addition increased *in vitro* aroma release, but this increase was not sufficient to induce differences in aroma release in the nasal cavity of subjects and thus in aroma perception. This could be explained by (i) differences in physicochemical parameters, too small to induce differences in aroma perception; (ii) trigeminal perception due to CO_2 that mask aroma perception; or (iii) the complexity of a carbonated in comparison with a non-carbonated product, inducing more difficulties for the panelists to assess the product.

This study contributes to a better understanding of the impact of composition (CO_2 and sucrose contents) on the physicochemical and sensory properties of drink matrices. The main effects that we observed were that CO_2 played a major role in aroma release. Flavor stripping played a preponderant role in aroma release in the nasal cavity of subjects and, consequently, in aroma perception. Nevertheless, sensory interactions, in particular with sugar, must be taken into account in the global aroma perception of soft drinks. Moreover, the results on temporal perception highlighted the dynamic evolution of aroma quality. Further experiments are in progress to validate our hypotheses. Finally, it might be worthwhile to consider the influence of some biological parameters and in particular the effect of carbonic anhydrase, in our system, during *in vitro* as well as *in vivo* measurements.

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Impact of swallowing on the dynamics of aroma release and perception during the consumption of alcoholic beverages

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Abstract

An integrated approach combining sensory analysis and physicochemistry was used to investigate the impact of swallowing on aroma release and perception. A panel of 10 people evaluated the dynamics of aroma perception during the consumption of a commercial flavoured vodka, using two protocols (spitting out or swallowing of the product) and the temporal dominance of sensations method. Nosespace analysis was simultaneously carried out by proton transfer reaction mass spectrometry to evaluate aroma release in their nasal cavity. Comparison of the results obtained with the two protocols highlighted significant differences in both the perception and the release of aroma: the swallowing of the product resulted in more complex perceptions, but decreased the dominance rates of aromatic attributes. Ethanol perception also had a high impact when the product was swallowed. These results may have implications for product formulation, depending on the way in which products are evaluated and/or consumed. Some relationships between sensory and physicochemical data have been established, particularly as concerns the temporal dimension of sensory and release phenomena, but the lack of knowledge concerning the variety and complexity of mechanisms continues to limit our understanding of the link between aroma release and perception.

Introduction

The overall perceived flavour of a food depends largely on the way in which volatile aroma compounds are released in the mouth and transported to the olfactory receptors in the nose during food consumption. Swallowing is particularly important in the drinking of beverages, which requires only limited oral manipulations, resulting in the product remaining in the mouth for only a short period [1, 3, 4].

In the field of alcoholic beverages, expert panels often make use of specific tasting techniques and various protocols to evaluate sensory properties. In particular, products are often tasted without swallowing, to limit the effect of ethanol ingestion. Perceptions are thus evaluated in conditions that do not really represent actual consumption conditions of a real tasting. The importance of swallowing for perception raises questions about the possible influence of tasting conditions on perception of the organoleptic properties of the product. However, this question has never before been addressed.

The aim of this study was to quantify the impact of tasting protocol (with or without swallowing of the product) on aroma release and perception in the case of a commercial flavoured vodka, through a combination of sensory and instrumental dynamic methods.

Experimental Methods

Product

The alcoholic beverage used in this study was a commercial, flavoured vodka (75 mL bottle, 40% v/v ethanol). A three-fold dilution was applied to the product throughout this study to reduce the ethanol content of samples. GC-MS analysis of the product extract identified 23 key aromatic components.

Drinking protocols

Panellists were served 5 mL of the beverage in a 70 mL hermetically sealed cup at room temperature (20°C). Panellists were asked to put the total amount of product in the mouth and to hold it there for 10 s while making tongue movements. They then had to spit the product out (protocol 1) or swallow it (protocol 2).

Sensory analysis

Sensory analysis was performed by the temporal dominance of sensations method [2]. A list containing three aroma attributes ("fruity", "green", "fatty") and one trigeminal attribute ("warm") was proposed to panellists to describe product perception. Dominance rates during consumption were calculated, by attribute, for each attribute and each protocol, generating TDS curves

PTR-MS measurements of *in vivo* release

The *in vivo* release of aroma compounds was characterized simultaneously to TDS measurements using a high-sensitivity PTR-MS instrument. The drift tube was thermostatically controlled (60°C) and operated at a set voltage of 600.1 (± 0.4) V. Nosespace air was sampled *via* the two inlets of a stainless steel nosepiece, which were inserted into the nostrils of the panellists (one on either side). The system was fixed on glasses to allow the panellists to drink reasonably normally.

The air in the room was first analysed for 10 s. The sampling device was then positioned in the two nostrils and the panellists were asked to breathe regularly for 30 s (breath analysis). They were then asked to put the entire sample into the mouth and to keep it there for 10 s whilst making tongue movements before either swallowing it or spitting it out. For data analysis, maximal intensities (I_{max1} and I_{max2}), times at which I_{max} occurred (t_{max1} and t_{max2}) and areas under the curve (AUC_1 and AUC_2) were extracted from each individual release curve and for each phase of product consumption.

Results

The effect of swallowing on temporal perception

When the product was spat out, a "fruity" note was perceived as the only dominant sensation, from the beginning of consumption and continuing for 47 s. Two peaks in the dominance rate of this attribute were detected, and a trough occurred just after the product had been spat out.

When the product was swallowed, perceptions became more complex, with the appearance of two other dominant attributes in addition to the "fruity" note. The "fruity" note was the first perceived,

for a period of 10s beginning at the start of consumption. Just after swallowing, a "warm" note was perceived as dominant for a period of 12 s, after which it was immediately replaced by a "fruity" note lasting 16 s. Finally, a "green" note was perceived as dominant after 50 s of consumption, over a period of 5 s. In neither protocol was a "fatty" note recorded as dominant by the panellists at any time. The dominance rate of the "fruity" note was lower when the product was swallowed than when it was spat out. All these results suggest that the swallowing event affects sensory perceptions, particularly in terms of dominance rates and dominant attribute sequences (over time).

Effect of the swallowing event on *in vivo* release kinetics

The shape of the release kinetics curve was ion-dependent, with differences observed in release intensity, release rate and persistence. The release of some fragments began immediately after the product was placed in the mouth and release remained of limited intensity, but with unlimited duration (signal persistence) (ion *m/z* 46). For ions *m/z* 47, 83, 117 and 131, a high initial rate of release was observed just after the swallowing event. The intensity of the signal was ion-dependent, with the ion *m/z* 47 being the most strongly released. For these fragments, the shape of signal decrease after the start of swallowing was also ion-dependent. For some ions, the signal persisted, with a slow return to initial levels (ions *m/z* 47 or 83). For others, decrease rates were high and further peaks appeared at each new swallowing event (whether the product was initially swallowed or not) (ions *m/z* 117 or 131). These patterns were observed for all the 10 panellists in spite of high levels of inter-individual variability.

When release parameters were concerned, swallowing resulted in a more intense release of aroma than spitting out for ions *m/z* 47 (related to ethanol) and *m/z* 55. The amount of ions released was greater when the product was swallowed than when it was spat out for ions *m/z* 47 and *m/z* 83. Finally, the time at which intensity was maximal was significantly earlier with swallowing than with spitting out, for ions *m/z* 55 and *m/z* 117. Thus, the swallowing of the product induced a more intense and earlier release of larger amounts of aroma compounds than obtained with spitting out, but only for a limited number of ions.

Discussion

The main significant differences between the two protocols tested, in terms of both sensory perception and instrumental data, are summarised in Table 1.

The "fruity" note, identified as dominant very early in consumption (from 5 s), seemed to be the characteristic note of this type of product, regardless of the protocol used. The definition of this attribute is broad and may relate to several aroma compounds present in the product (esters, lactones, ketones, etc) and released rapidly after the product was placed in the mouth. The greater complexity perceived when the product was swallowed may be attributed partly to sensory phenomena, such as the stimulation of a larger number of sensory receptors over a longer period of time. However, it may also be due to physicochemical factors, as ethanol release was significantly greater when the product was swallowed than when it was spat out. The occurrence of a dominant "green" note at around 50s when the product was swallowed may also reflect physicochemical phenomena, including the release of fragments *m/z* 55 and 83 (originating mostly from aroma compounds responsible for the "green" attribute), which were strongest when the product was swallowed. This note was perceived at the beginning of consumption, despite the presence of a maximal release peak at around 20 s, probably masked by other attributes ("fruity" and/or "warm"). However, these fragments decreased slowly and seemed to be more persistent than the others, potentially accounting for the delayed perception of the "green" note (which

could be explained by specific physicochemical interactions between aroma compounds and pharyngeal and/or oesophageal mucosa and/or by sensory interactions).

Table 1: Summary of the sensory and instrumental results obtained in this study. Only significant data are listed. Symbols "-" and "+" are used to compare signal level between the two protocols.

		Product swallowed	Product spat out
Sensory data	Dominant perceptions and sequence	"fruity"/ "warm"/"fruity"/"green"	"fruity"
	Dominance rate	- "fruity" + "warm" + "green"	+ "fruity" - "warm" (not significantly dominant) - "green" (not significantly dominant)
	Mean time and mean duration parameters	No significant difference	
Instrumental data	I_{max2} and AUC_2, *m/z* 47	+	-
	I_{max2}, *m/z* 55	+	-
	AUC_2, *m/z* 83	+	-
	t_{max2}, *m/z* 55 and 117	-	+

We found that the swallowing event affected aroma perception during beverage consumption and that both sensory and physicochemical phenomena were involved. This conclusion may have implications for product formulation, depending on the way in which products are evaluated and/or consumed. The spitting out of the product is a useful protocol for the development of alcoholic products because it allows the taster to focus on aroma perception and limits the effects of ethanol ingestion. However, the results obtained must be interpreted with caution, as this protocol does not correspond to the way in which beverages are actually consumed. It is also important to note that although some relationships have been proposed, it remains difficult to relate sensory and instrumental data, due to the variety and complexity of the phenomena involved (physiological, sensory, physicochemical, etc).

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Application of Chemical Ionization by H3O+ or NO+ and subsequent Collision Induced Dissociation of major product ions to selective on-line detection of sesquiterpenes and monoterpenes

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Abstract

Selective detection of Biogenic Volatile Organic Compounds (BVOC) is important due to the fact that individual BVOCs can affect atmospheric chemistry in different ways. However, existing on-line Chemical Ionization Mass Spectrometry (CIMS) techniques for BVOC quantification suffer from the difficulty to discriminate isomeric compounds.

Therefore, the feasibility of selective detection of a series of seven sesquiterpenes (SQT) and six monoterpenes (MT) using collision-induced dissociation (CID) of major product ions of their reactions with H_3O^+ and/or NO^+ has been investigated in a Flowing Afterglow Tandem Mass Spectrometer (FA-TMS). These BVOCs were chemically ionized by H_3O^+ or NO^+ reagent ions in the FA, resulting in major product ions at *m/z* 205 (SQT + H_3O^+), *m/z* 204 (SQT + NO^+) and *m/z* 136 (MT + NO^+). These ions were subsequently subjected to CID with Ar atoms in the TMS collision cell

Although the fragmentation of protonated SQT (*m/z* 205) resulted in fragment ions at the same *m/z* values for all SQT investigated, differences in fragment ion intensities have been found between SQT. This enables SQT distinction based on intensity ratios at certain defined collision energies. The fragmentation of SQT molecular ions (*m/z* 204) resulted in the identification of tracer-fragment ions for α-cedrene, δ-neoclovene, isolongifolene and α-humulene. Finally, fragmentation of MT molecular ions (*m/z* 136) has also revealed some tracer-fragment ions for individual compounds or groups of compounds. Consequently, chemical ionization by NO^+, followed by MS/MS seems to open a way for selective quantification of BVOCs in mixtures.

Introduction

A considerate quantity of global non-methane biogenic volatile organic compound emissions can be attributed to isoprenoids. Of these isoprenoids, isoprene is globally emitted in largest quantities but, dependent on the vegetation species and biotic and abiotic factors, monoterpene (MT, $C_{10}H_{16}$) and sesquiterpene (SQT, $C_{15}H_{24}$) emissions can be considerable as well. Within the class of isoprenoids, large differences have been observed between individual compounds regarding oxidation mechanisms, oxidation products formed and secondary organic aerosol (SOA) formation. Consequently, compound-specific concentration and flux measurements are necessary for accurate modeling of isoprenoid atmospheric chemistry and their impact on air quality and global climate.

Gas Chromatography Mass Spectrometric (GC-MS) and Chemical Ionization Mass Spectrometric (CIMS) techniques are commonly used to detect and quantify isoprenoids. CIMS techniques, such as Proton Transfer Reaction Mass Spectrometry (PTR-MS), have a high sensitivity and allow fast on-line measurements of reactive BVOCs such as SQT. However, an important disadvantage to CIMS techniques using H_3O^+ reactant ions is their impossibility to distinguish isomeric compounds. Improvements to selectivity can possibly be made by using other CI reagent ions such as NO^+ (e.g. [1], [2]) and/or the application of MS/MS techniques for the search for compound-specific fragmentation schemes obtained under controlled conditions ([3], [4]).

Recent collision induced dissociation (CID) experiments on a series of protonated MT (*m/z* 137) and two protonated SQT (*m/z* 205) by Müller *et al.* [4] have shown promising results concerning differentiation between isomeric protonated species. For further verification of the applicability of this approach to SQT differentiation, CID of a larger selection of SQT must be evaluated.

Therefore, in this study, the proton transfer product (*m/z* 205) from the reaction of H_3O^+ of seven different SQT and the charge transfer products of the reactions of NO^+ with six MT (*m/z* 136) and seven SQT (*m/z* 204) have been subjected to CID in a FA-TMS in view of their respective selective detection with H_3O^+ and NO^+.

Experimental Methods

The isoprenoids investigated in this research are the MT α-pinene, β-pinene, Δ^3-carene, γ-terpinene, limonene and myrcene, the SQT aromadendrene, β-caryophyllene, α-cedrene, α-humulene, isolongifolene, longifolene and δ-neoclovene.

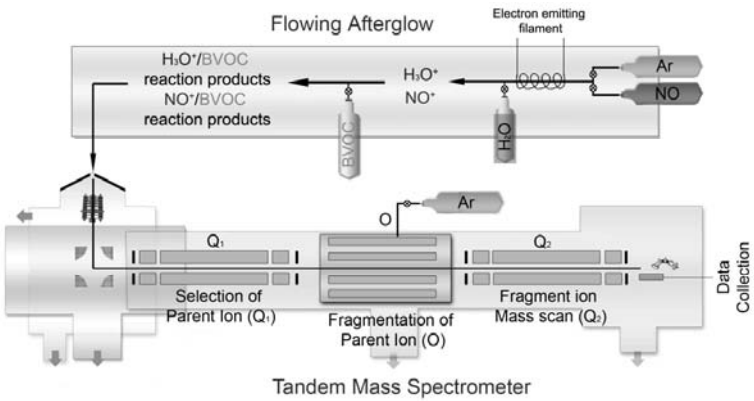

Figure 1: Schematic representation of the FA-TMS instrument

The instrument used in this experiment is a FA-TMS (see figure 1), consisting of a home-made Flowing Afterglow reactor coupled to a custom-designed Tandem Mass Spectrometer [3]. A controlled quantity of the isoprenoid neutral reactant is introduced in the FA and the reaction between the H_3O^+ or NO^+ reagent ion and the neutral takes place in the FA in Ar buffer gas at thermal conditions (295 K).After reaction, all product ions are sampled into the TMS. The CI product ion of interest is selected by a first quadrupole and subsequently enters the octupole collision cell where it can undergo CID. The collision cell is filled with Ar collision gas at a pressure of 0.11 Pa and depending on the collision energy in the center-of-mass frame (E_{CM}),

determined by the pole bias of the octupole and the stopping potential (determined by retardation potential analysis [3]), one or more fragments can be produced. The second quadrupole is used as a mass analyzer and after detection with a secondary electron multiplier, a fragmentation spectrum is obtained. When repeating this process for several E_{CM} values, fragmentation yields as a function of E_{CM} are obtained.

Results and discussion

CID of protonated SQT at *m/z* 205

A lot (30+) of different fragment ions were obtained from the CID of protonated SQT. To classify these fragments, fragment families were created of which each family gathered fragment ions separated by a CH_2 unit. This resulted in the identification of five separate families. Fragment ions found at an $E_{CM} < 2$ eV were found to correspond well to major fragments ions found for other techniques such as SIFT-MS and PTR-MS when introducing pure SQT.

Although our results were not corrected for mass discrimination, fragmentation fractions for protonated α-humulene at a *m/z* value of 0.68 eV are remarkably similar to the fragmentation fractions of α-humulene obtained by Müller *et al.* [4] in a PTR-LIT and a QqQ-MS at 12 V collision cell offset (U_{CC}). In comparison to the findings of Müller *et al*, no tracer fragment ions were found for the SQT studied and only differences in selected intensity ratios, such as I_{69}/I_{123}, I_{121}/I_{123} and I_{83}/I_{135}, allow to respectively discriminate isolongifolene, α-cedrene and aromadendrene from the other SQT.

CID of the NO^+/SQT charge transfer product at *m/z* 204

The fragmentation patterns of SQT molecular ions provide powerful information for the selective detection of SQTs.

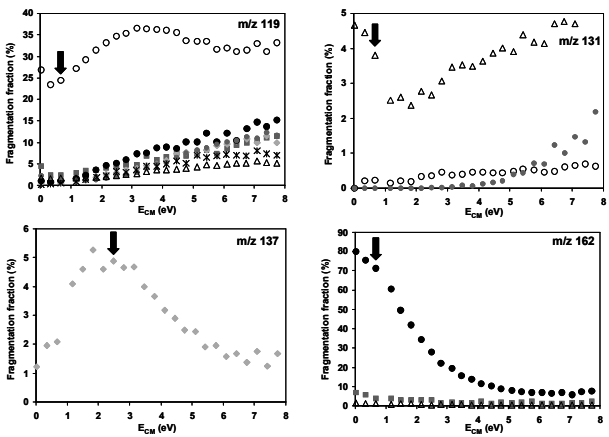

Figure 2: Fragmentation fractions (%) of ions at m/z 119, m/z 131, m/z 137 and m/z 162 as a function of ECM for break-up of protonated α-cedrene (○), δ-neoclovene (●), aromadendrene (■), longifolene (◆), isolongifolene (●), β-caryophyllene (∗) and α-humulene (△). Arrows indicate ECM values at which selective detection of a-cedrene (m/z 119), a-humulene (m/z 131), isolongifolene (m/z 137) and d-neoclovene (m/z 162)

At well-chosen collision energies, some tracers can be found. A fragment ion is considered as a tracer of a specific SQT if its fragmentation fraction is at least ten times higher than for the other SQTs studied. This is the case for ions at 0.7 eV (*m/z* 119) for α-cedrene, 0.7 (*m/z* 162) and 6.1 eV (*m/z* 83) for δ-neoclovene, 2.5 eV (*m/z* 137) for longifolene and 0.7 eV (*m/z* 131) for α-humulene. The fragmentation fractions as a function of ECM for the ions at *m/z* 119, 131, 137 and 162 are given in figure 2. Due to the often low fragmentation fractions of the tracer ions, the sensitivity of the instrument is a limiting factor.

CID of the NO^+/MT charge transfer product at *m/z* 136

In comparison with the SQT, some tracers for individual MT were found at well-chosen collision energies for fragmentation of the MT charge transfer product at *m/z* 136. Tracers of limonene were found at 5.0 eV (*m/z* 68) and 4.6 eV (*m/z* 95).

Other tracer ions could be found under particular conditions. As an example, at 2.7 eV, ions at *m/z* 92 can only be used as sensitive tracer ions for α-pinene if Δ^3-carene and limonene are not present in the mixture. Similarly, Δ^3-carene can only be sensitively monitored at 0.9 eV via the ions at *m/z* 121 when the only other MT in the mixture is α-pinene.

Acknowledgements

The authors gratefully acknowledge the financial support of the Belgian Federal Science Policy (research projects MO/35/022 and MO/35/026) and the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen).

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The PTR-QMS 300 - a universal tool for industrial and research applications

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Abstract

The PTR-QMS 300 (Figure 1) is the replacement for the old Compact PTR-MS. It consists of the established Proton Transfer Reaction (PTR) chamber connected via a lens region to a quadrupole mass spectrometer. Two turbomolecular and a pre-vacuum membrane pump provide the necessary vacuum conditions. Operation of the machine is done with the help of an embedded computer. This computer is continuously monitoring the system status and therefore preventing it from damages e.g. by shutting down the voltages in case of a vacuum problem. Additionally the computer allows for a very user friendly operation of the system. A touch screen allows for easy handling of the instrument. The software can be easily adapted to meet the specific requirements for industrial applications. On the other hand it can be used as a research instrument with control over all relevant parameters.

Figure 1: Picture of the newly developed PTR-QMS 300

As an example, in the framework of the EDA JIP-FP "GUARDED" project this machine will be placed on top of a robot. The aim of this project is to develop a remote controlled platform for the sniffing of suspicious persons and dangerous areas and the identification of possible harmful substances. To ensure an easy operation process a highly user-friendly software was developed.

This enables the operator to work with the machine without specific knowledge on chemistry or physics. The result is displayed directly on the touch screen or a connected laptop computer. There it is indicated which of the pre-set substance have been detected and at which threat level.

For monitoring in industrial applications [1] a pre-set of desired substances can be set and monitored without deeper knowledge of the system. The results are displayed at the monitor (see Figure 2) and if desired alarm, e.g. when exceeding defined concentration levels, is triggered.

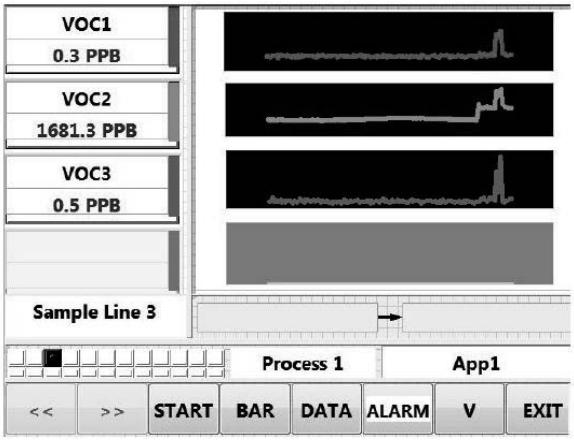

Figure 2: Example of display for industrial monitoring purposes

Acknowledgement

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Exploring the effects of *E/N* and humidity on the fragmentation of green leaf volatiles (GLVs) in a PTR-TOF-MS

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Abstract

The effects of *E/N* and sample humidity on the identification and quantification of green leaf volatiles (GLVs) by PTR-TOF-MS have been investigated. The compounds examined in this work were hexanal, 1-hexanol, trans-2-hexenal, cis-3-hexenal, cis-3-hexenol, trans-3-hexenol, trans-2-hexenol, cis-3-hexenyl acetate and hexyl acetate. Changes to *E/N* had a considerable effect on the product ion branching ratios for each of the compounds. The results demonstrate that specificity can be enhanced by modulating *E/N*. The product ion branching ratios were affected by sample humidity, with less fragmentation observed as humidity increased. Sensitivity was found to increase linearly with sample humidity. These effects reinforce the need to accurately characterize the ion chemistry in the drift tube for quantitative investigations. The work has provided detailed information about the operating characteristics of our PTR-TOF-MS and the data should be a useful aid to future quantitative PTR-MS studies of GLV emissions from plants.

Introduction

To accurately quantify VOCs by PTR-MS it is essential that the product ion(s) generated from each analyte are known. Instrumental and environmental conditions can have a considerable effect on the products observed. Of particular importance is the ratio *E/N* which determines the mean centre-of-mass collision energy between reactant ions and neutrals and the extent of product ion fragmentation. Most investigations are performed at fixed *E/N* but it is sometimes useful to adjust *E/N* to improve specificity. Several PTR-MS studies have identified situations where it is possible to differentiate isobaric/isomeric ions by modulating *E/N* [1, 2, 3]. In these circumstances it is essential that the ion chemistry in the drift tube is well characterized if PTR-MS is to be used for quantitation. This includes an assessment of the effects of sample humidity. Humidity can affect PTR-MS measurements by altering the degree of hydration of the reagent ion.

The emission of green leaf volatiles (GLVs) from plants has attracted interest in recent years because of their potential effect on chemistry in the atmosphere [4]. GLVs present a particular challenge to PTR-MS because they are structurally similar. GLVs are also highly susceptible to fragmentation following ionization in a PTR-MS [5]. Previous studies illustrate how difficult it is to distinguish GLVs by PTR-MS without additional analytical capability [5-10].

The principal objective of this work is to establish what effects *E/N* and humidity have on our ability to measure and quantify GLVs. We will also explore whether adjustments in *E/N* could be used to improve the specificity of GLV analysis. This should provide detailed information about the operating characteristics of our PTR-TOF-MS and the data will be a useful aid to future quantitative studies of GLV emissions from plants.

Experimental Methods

The PTR-TOF-MS used for this work (Figure 1) is a modified version of that described in [11]. The hollow cathode ion source and the drift tube have been substituted with equivalent components made by the manufacturer of the TOF-MS (Kore Technologies, Ely, Cambridge).

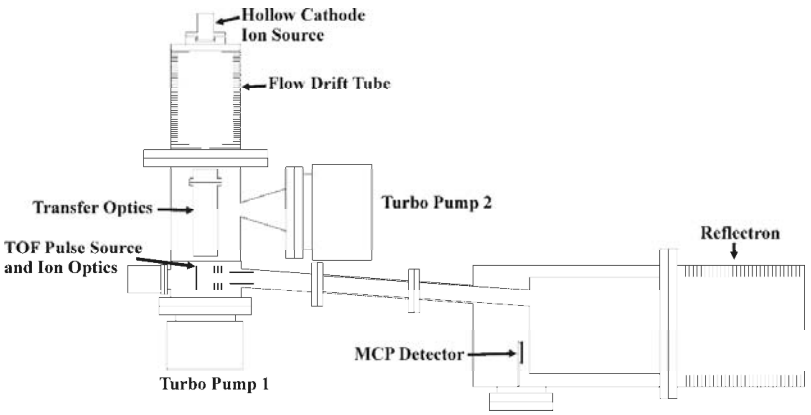

Figure 1: Schematic of the PTR-TOF-MS (not to scale).

Pure samples of the GLVs were obtained from Sigma Aldrich and used without further purification. The GLVs were introduced to the PTR-TOF-MS from a permeation system and diluted in hydrocarbon free air. For the humidity experiments the diluent gas was humidified by bubbling it through a Dreschel bottle filled with de-ionised water. Product ion branching ratios were recorded with a drift tube pressure of 1.20 ± 0.01 mbar and a potential difference across the drift tube between approximately 300 V and 490 V corresponding to *E/N* values from 105 and 175 Td. Humidity dependent calibrations were measured at 167 Td.

Results and Discussion

It is clear from the results that GLVs are highly susceptible to fragmentation, with multiple products observed across all values of *E/N*. As demonstrated by cis-3-hexenol in Figure 2, greater fragmentation is observed at high *E/N*. The break-up of the protonated ions is remarkably similar for each or the analytes with water the most common loss product. Although many of the GLVs generate the same product ions and are thus indistinguishable, the product ion distributions are often quite different, particularly at low *E/N*. These differences could be exploited to enhance the specificity of GLV analysis.

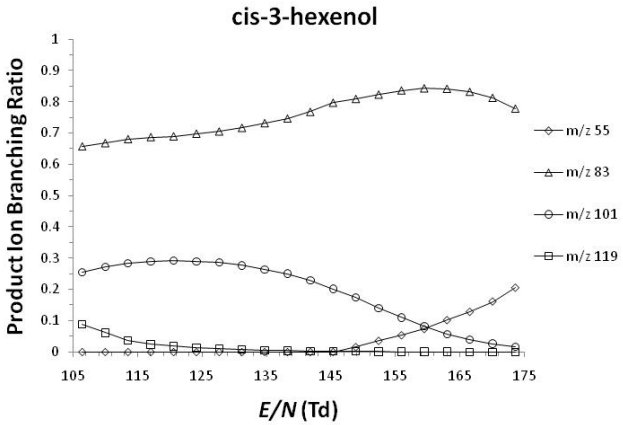

Figure 2: Product ion distribution as a function of E/N for cis-3-hexenol in dry air.

Sensitivities for the GLVs were typically between 10 and 25 ncps $ppbv^{-1}$ and increased linearly as the relative humidity of the sampled air was increased. Product ion branching ratios were also affected by changes in humidity, presumably due to changes in the reagent ion distribution affecting the kinetics and dynamics of reactions in the drift tube.

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Application of PTR-MS for measuring odorants from livestock production

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Abstract

Intensive pig production is a source of offending malodorous compounds including carboxylic acids, phenols, indoles, aldehydes, ketones, amines and volatile reduced sulfur compounds [2, 4, 5, 6]. These odorants adversely influence air quality in the vicinity of the sources [1] Little knowledge exists on factors influencing the variability of odorant emissions from intensive pig production facilities. This is mainly due to the lack of time-resolved quantitative methods for measuring the full range of known odorants. Recently, proton-transfer-reaction mass spectrometry (PTR-MS) has been employed for monitoring emissions of odorants and has been demonstrated to be very suitable for this purpose [3]. Quantitative and time-resolved results for protonated ions representing H_2S, volatile organic sulphur compounds, organic amines, volatile carboxylic acids, carbonyls, phenols, and indoles can be obtained. Results from PTR-MS measurements of odorant emissions from finisher pig houses and a 1:6 pig house scale model are presented and discussed. One set of measurements were performed at an experimental full-scale pig section with mechanical ventilation. The data sets include field measurements during variable air exchange rates and temperatures, during finisher growth, and during emptying of the slurry pit. A pronounced diurnal variation in emissions of odorants from the pig section was observed with peaks in daytime coinciding with high ventilation rates, elevated room temperature, and increased animal activity. Highest emission rates were observed for H_2S and carboxylic acids. Compound assignments were obtained by comparison with parallel measurements by thermal desorption GC/MS and GC with sulphur-specific chemiluminescence detection, supported by isotope patterns and correlations of masses. Quantification was based on authentic reference standards as well as calculations of rate constants.

In order to specifically investigate the effects of air exchange rate without covariance of other factors, a scale model containing pig slurry was used under isothermal conditions. Four ventilation rates were used to measure concentration variations at inlet, outlet, and slurry pit of the model. For most compounds emissions were positively correlated with air exchange rate indicating an increased mass transfer rate at increased air velocity close to the liquid slurry surface as expected from theory. However, acetic acid emission was negatively correlated with ventilation rate and H_2S emission was independent of ventilation rate. This indicates that increased air velocity enhances the penetration of oxygen into the largely anaerobic slurry and, hence, increases surface oxidation of certain compounds. In addition, the temporal evolution of emissions following stirring was investigated. For several odorous compounds, emissions were observed to decrease strongly with time after stirring, which is mainly ascribed to limitation of diffusion to the surface by establishment of a natural floating layer.

Comparison of full scale and scale model measurements indicates that carboxylic acids are mainly emitted from the animal room (soiled surfaces) and only to a lesser degree from the slurry.

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Evaporating Liquid Samples for Analysis with PTR-MS

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Abstract

We present a method for measuring liquid samples with the PTR-MS by using a spray to convert the liquid into the gas phase. Advantages over headspace measurements concerning compounds with high Henry's law constants could be demonstrated.

Introduction

As PTR-MS is limited to the detection of compounds in the gas phase only, analyzing liquids requires additional measures. Taking samples of the headspace above a liquid can yield good results, but many effects influence the correlation of headspace and liquid concentration. Thus we studied the possibility of using a nozzle to transfer the whole sample into the gas phase, circumventing the equilibrium between gas and liquid concentrations.

Experimental Methods

Setup

The liquid sample is injected together with a dilution gas to form a spray. The gas droplets subsequently evaporate. The resulting gas mixture is then analyzed by PTR-MS.

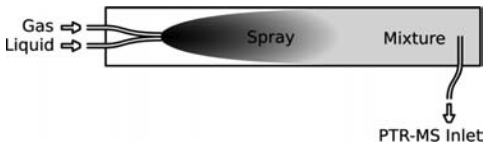

Figure 1: Setup for evaporating liquids for the measurement with PTR-MS.

Measurements

Acetone and acetic acid were diluted in water in different concentrations, both with the same molar rations of 3ppm, 6ppm and 9ppm. This mixtures were injected with a constant rate into a constant air flow. The normalized signals are displayed in Figure 2 (left).

Results and Discussion

We observe that the concentrations of both compounds increase with increasing sample concentration.

Furthermore, the signals of the different substances take a different amount of time to equilibrate when the concentration is changed. This equilibration time depends on their polarity, which causes them to stick to the walls of the inlet lines.

In Figure 2 (right) the signal of acetone vs. acetic acid is plotted. The ratio between the signals is close to 1, which means that both compounds are detected with a similar sensitivity. This is in contrast to the concentration of a compound in the headspace, that depends critically on its Henry's law constant, which is orders of magnitude apart for acetone (30 $mol \cdot kg^{-1} \cdot bar^{-1}$ [1]) and acetic acid (5400 $mol \cdot kg^{-1} \cdot bar^{-1}$ [1]).

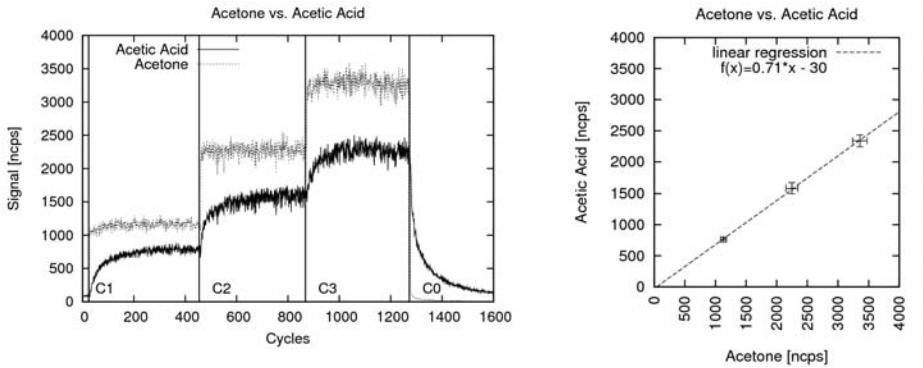

Figure 2: (left) Signal of acetone (m/z 59) and acetic acid (m/z 61 + m/z 43, fragment) for different concentrations. (right) Signal of acetone vs. acetic acid. The slope close to 1 indicates that the sensitivity for both compounds is almost akin.

Conclusions

Our findings show, that the presented method is suitable to vaporize a liquid sample and that this method can dramatically increase the sensitivity over headspace measurements for compounds with high Henry's law constants. Moreover, this technique can also be used to produce inexpensive standard-gas mixtures from liquids in order to calibrate various gas-analytical instruments.

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Determination of gas phase Isocyanate using proton transfer reaction mass spectrometry

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Objective

The aim of the present study was to develop a method for the direct monitoring of airborne gas phase isocyanates. Isocyanates are hazardous and allergenic compounds that are commonly used in the industry for manufacturing of polyurethane, which is applied frequently in lacquers, elastomers, coatings and in soft and rigid foams. The study, performed in a climate chamber, focus on the direct monitoring of highly reactive isocyanates: isocyanic acid (ICA), methyl isocyanate (MIC), ethyl isocyanate (EIC), phenyl isocyanate, hexamethylene diisocyanate (HDI) and toluene diisocyanate, using proton transfer reaction mass spectrometry (PTR-MS) [1].

Experimental Methods

Airborne isocyanates were introduced into the ion source by a heated inlet tubing (60°C) of PEEK at a flow rate of 0.5 l /min. The PTR-MS is based on ionization using protonated water and the positively charged protonated molecular ions were monitored by selected ion recording. The generation of ICA and MIC was achieved through thermal degradation of urea and 1,3-dimethylurea, respectively (Figure 1) [2]. The other isocyanates studied were generated by liquid and gas permeation techniques [3]. Comparative measurements were made by sampling in impinger flasks containing dibutyl amine (DBA) as the reagent and the isocyanate DBA derivatives were determined by LC-MSMS [4; 5].

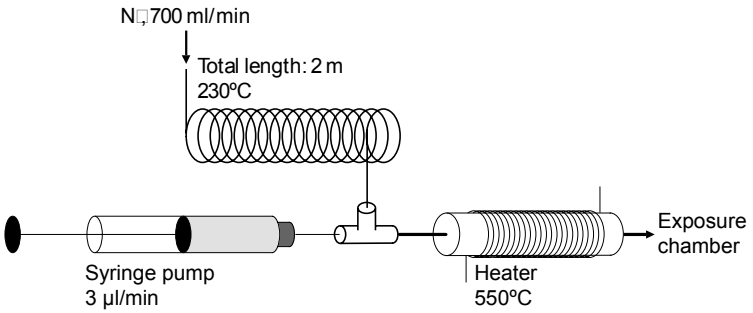

Figure 1. Schematic picture of the thermal degradation apparatus for generation of ICA and MIC. A flow of 3 µl min^{-1} of 1.0-1.5 mol l^{-1} urea and dimethylurea water solution was sprayed into a heated zone, using pre-heated nitrogen. The formed degradation products were ICA, ammonia, MIC and methylamine.

Results

Reproducible measurements were obtained and the drift in response was <10% during a 12 month period. When comparing the response for the LC-MSMS with the PTR-MS data, linear responses (R2 = >0.99) for all tested isocyanate (0-100 ppb) were obtained. The protonated molecular ions have a detection limit in the low ppb level. With the exception for EIC and HDI were the protonated molecular ions were the most abundant ions [6]. The PTR-MS response was influenced by the air humidity (Figure 2) [2].

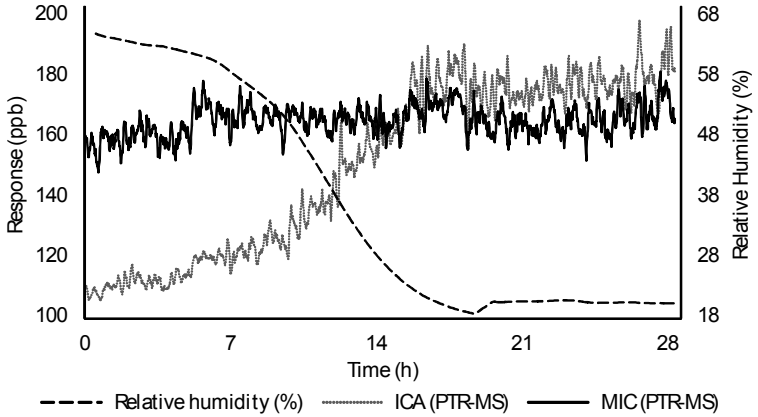

Figure 2. The PTR-MS response for ICA increased by >50%, relative to impinger measurements during a humidity decrease inside the climate chamber (65% to 20% RH, measured by a Testo 645, GmbH & Com Germany). Air concentrations (ICA = 190 ppb, MIC = 170 ppb), was determined by triplicate impinger samples (n=18) and LC-MSMS analysis during the 28 hours test, with a relative standard deviation of 11 and 3 % for ICA and MIC, respectively.

Conclusions

The developed method enabled sensitive and selective time resolved measurements of airborne isocyanates for several weeks. Measurements below current occupational exposure limit values were achieved.

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New acquisition and automation possibilities for PTR-QUAD and PTR-TOFMS measurements

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Abstract

In the last years the variety of PTR-MS usage has been significantly expanded. Also the number of different instrument types as well as the number of different reaction conditions (SRI) has been expanded. Due to this expansion the need of user tailored software solutions has been increased. In addition to the Ionicon built user tailored software solutions it was also a goal to give the existing and new PTR-MS users the possibility to build their own solution for their special needs. The fundamental start for this software feature revolution was the recently developed possibility in the PTR-MS technique called SRI (Switchable Reagent Ions) [1] which gave a big push in the PTR-MS measurement possibilities. For optimal usage it was also necessary to improve the PTR-MS control software components. The main goal of the new software evolutions was on one side the easy usage of the acquisition process. The other main feature is the flexibility. Especially the extended measuring features of PTR+SRI-MS systems showed the needs of flexible automation for different measurement tasks. In earlier PTR-MS versions it was also possible to use the sequencer for tailored measuring tasks but it was complicated and relatively inflexible. All new versions of PTR-MS software (from version 2.6 of PTR-MS control for Quadrupole instruments and from version 2.3 of PTR-Manger for Time Of Flight) gives you language independent API (advanced programming interface) functions to control most of the parts of PTR-MS systems. Especially for advanced users it is often interesting to switch between different primary ions, change the energetics of the reactions or do some external automation by using analog or digital outputs. These outputs can either be the fundamental extras of every PTR-MS system or additional outputs which have been added by the usage of the Ionicon options box which adds nearly unlimited number of analog out- and inputs to any PTR-MS solution. This option box can also be added as a standalone instrument to any other measurement solution where easy programming and flexibility is a goal.

All the API calls are available either in unmanaged dll or in managed dll versions for .NET usage. The easiest way to use it is by using a scripting language like the free LUA language. But also the development of complex tasks by the usage of a powerful software development suite like Visual Studio is possible. The probably easiest possibility for usage in laboratory environment is the usage of the API commands as pre-built LabVIEW vi's which gives the possibilities to automate your tasks within minutes.

All the API communication is based on the TCP/IP protocol which enables it for the usage over a network. This gives you the possibility to control the main program from different locations and also pick up current data from the instruments.

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Biotic, abiotic and management controls on methanol exchange above a temperate mountain grassland

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Abstract

Methanol (CH_3OH) fluxes were quantified above a temperate mountain grassland, managed as a hay meadow, in the Stubai Valley (Tyrol, Austria) during the growing seasons 2008 and 2009. Half-hourly methanol fluxes were calculated by means of the disjunct eddy covariance (vDEC) method using 3-dimensional wind data from a sonic anemometer and concentrations of methanol measured with a proton-transfer-reaction mass spectrometer (PTR-MS). Management events were found to represent the largest perturbations of methanol exchange at the studied grassland ecosystem: peak emissions of up to 144.5 nmol m^{-2} s^{-1} were found during/after cutting of the meadow (Fig. 1) reflecting the wounding of the plant material and subsequent depletion of the leaf internal aqueous methanol pools. After the application of organic fertilizer elevated methanol emissions of up to 26.7 nmol m^{-2} s^{-1} were observed (Fig. 1), likely reflecting enhanced microbial activity associated with the applied manure. During (undisturbed) mature and growing phases methanol fluxes exhibited a clear diurnal cycle with close to zero fluxes during nighttime and emissions, up to 10 nmol m^{-2} s^{-1}, which followed the diurnal course of radiation and air temperature. Simple and multiple linear regression analyses also revealed air temperature and radiation as the dominant abiotic controls, jointly explaining 47 % and 70 % of the variability in half hourly and daily methanol fluxes. In contrast to published leaf level laboratory studies [1, 2, 3], the surface conductance and the daily change in the amount of green plant area, used as ecosystem scale proxies for stomatal conductance and growth respectively, were found to exert only minor biotic controls on methanol exchange. We suggest this discrepancy to result from differences in spatial and temporal scale of flux as opposed to leaf-level enclosure measurements and controlled laboratory environments as opposed to real-world field conditions. In order to close the apparent gap that exists in transferring leaf-level laboratory knowledge to *in situ* conditions at the ecosystem scale [4], which hampers the development and parameterization of ecosystem models, concurrent studies on leaf/soil and ecosystem scale methanol exchange under field conditions are advocated.

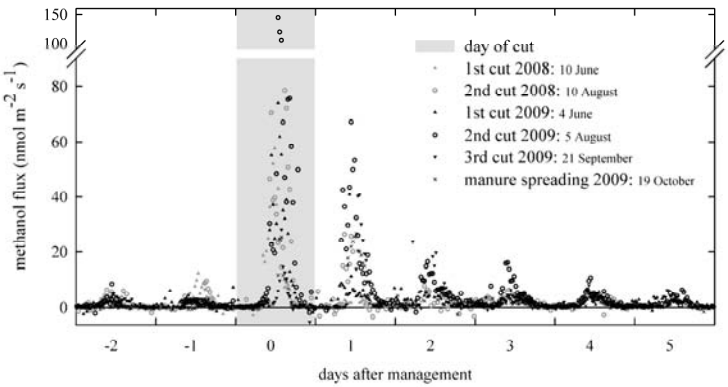

Figure 1: Methanol fluxes before, during and after management events. Data points represent half-hourly fluxes.

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A deuterium-labeling study on the reproduction of hydronium ions in the PTR-MS detection

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Abstract

The detection sensitivities of proton transfer reaction mass spectrometry for ethanol, 2-propanol and acetic acid were examined systematically at five different kinetic energies. The detection sensitivity for acetic acid was in good agreement with the sensitivities calculated from the experimentally and theoretically obtained rate constants for the reaction of H_3O^+ with acetic acid. However, the detection sensitivities for ethanol and 2-propanol were quite small compared with the calculated values. In deuterium-labeling studies, the formation of H_2DO^+ ions at *m/z* 20 in the reactions of H_3O^+ with deuterium-labeled ethanols, CD_3CH_2OH and CH_3CD_2OH, and deuterium-labeled 2-propanol, $(CD_3)_2CHOH$, was clearly observed, whereas the formation of H_2DO^+ was not observed in the reaction of H_3O^+ with $CD_3C(O)OH$. We concluded that the difference between the experimental and calculated detection sensitivities for ethanol and 2-propanol was attributed to the reaction channel that re-produced H_3O^+ ion during the reactions of H_3O^+ with ethanol and 2-propanol.

Introduction

Proton transfer reaction mass spectrometry (PTR-MS), which allows on-line detection of volatile organic compounds (VOCs) at trace levels in air is currently used in many areas of research, such as atmospheric chemistry, plant physiology and ecology, medical research, and food research. Proton transfer is a type of chemical ionization that enables soft ionization of chemical species that have a proton affinity higher than that of the reagent species (i.e., water):

$$H_3O^+ + VOC \rightarrow VOC{\cdot}H^+ + H_2O \qquad (1a)$$

Unlike gas chromatography, PTR-MS does not require any sample treatment such as drying or preconcentration, and therefore quantitative measurements of even oxygenated VOCs are possible.

Another property of PTR-MS is that the concentration of a detected VOC can be calculated from the following kinetic relationship, because the ionization reaction is an ion−molecule reaction:

$$[\mathrm{VOC}] \approx \frac{i(\mathrm{VOC}\cdot\mathrm{H}^+)}{k \cdot t \cdot i(\mathrm{H_3O}^+)} \qquad (2)$$

where $i(H_3O^+)$ and $i(VOC{\cdot}H^+)$ represent the count rates of the reagent ion, H_3O^+, and the product ion, $VOC{\cdot}H^+$, respectively; k represents the rate constant for the proton transfer reaction; and t represents the reaction time. This property is useful for some VOCs, the calibration of which is difficult. The reaction time, which is typically 10^{-4} s, can be determined from the H_3O^+ drift velocity and the length of the drift tube. The rate constants usually range between 1.5×10^{-9} and 4×10^{-9} cm^3 $molecule^{-1}$ s^{-1}, which are identical to collision limiting values. The rate constants can be obtained experimentally, for example, by means of selected ion flow tube mass spectrometry,

which supplies thermal rate constants, while they can be also derived theoretically. The agreement between the theoretical and experimental rate constants is within 25% in most cases.

For fragile VOCs at ionization, $i(\mathrm{VOC{\cdot}H^+})$ in Eq. (2) should be replaced with the sum of the count rates of the protonated molecule and any fragment ions:

$$\mathrm{H_3O^+ + VOC \rightarrow fragment^+ + other\ products} \quad (1b)$$

$$[\mathrm{VOC}] \approx \frac{i(\mathrm{VOC \cdot H^+}) + \sum i(\mathrm{fragment^+})}{k \cdot t \cdot i(\mathrm{H_3O^+})} \quad (3)$$

In the case of ethanol, the detection sensitivity of ethanol under dry conditions was determined to be 1.6 ± 0.1 normalized counts per second (ncps)/parts per billion by volume (ppbv), which is almost seven times less than that of methanol (10.6 ± 0.4 ncps/ppbv), although the rate coefficient of the reactions of H_3O^+ with ethanol has been reported to be the same with methanol (2.7×10^{-9} cm^3 $molecule^{-1}$ s^{-1}). The production of a fragment ion, $C_2H_5^+$, at *m/z* 29 was observed besides protonated ethanol, $C_2H_5OH{\bullet}H^+$, at *m/z* 47, but the contribution of the fragmentation process is not significant in the reaction of ethanol with H_3O^+.

In this paper, we discuss an agreement between the experimental and calculated detection sensitivities for fragile species, ethanol, 2-propanol, and acetic acid. We found the reaction channels that re-produced H_3O^+ ion during the reaction of H_3O^+ with ethanol and 2-propanol by detecting H_2DO^+ ions at *m/z* 20 produced in the reactions of H_3O^+ with deuterium-labeled ethanols (CD_3CH_2OH and CH_3CD_2OH).

Experimental Methods

We used a commercially available PTR-MS instrument (Ionicon Analytik). Briefly, H_3O^+ ions were produced from a pure water vapor flow of 7.8 sccm in a hollow cathode discharge ion source. The sample air was introduced into the drift tube at a flow rate of approximately 22 sccm and the drift tube pressure was held at 2.1 mbar. Temperatures of the sampling inlet and the drift tube were held at 105 °C. The drift tube (9.2 cm long) consisted of stainless steel ring electrodes, separated by Teflon rings for electrical isolation. The ring electrodes were connected to a resistor network, which divided the overall drift voltage into a homogeneously increasing voltage and established a homogeneous electric field inside the drift tube to avoid substantial formation of cluster ions, $H_3O^+{\bullet}(H_2O)_n$ (n = 1, 2, ⋯). In the drift tube, trace gases such as VOCs in the sample air were ionized by proton transfer reactions (reaction (1)). A fraction of the reagent ion, H_3O^+, and the product ions was extracted through a small orifice into a quadrupole mass spectrometer. The ions were detected by a secondary electron multiplier for ion pulse counting. The mass dependence of the transmission efficiency of the QMS was calibrated by the manufacturer.

The count rate of the reagent ion, H_3O^+, calculated from the count rate at *m/z* 21 ($H_3{}^{18}O^+$) multiplied by 500, was in the range (5–10) × 10^6 cps. The ratios of the ion intensity of $H_3O^+{\bullet}H_2O$ (*m/z* 37) to that of H_3O^+ were 0.016 at *E/N* = 108 Td and 0.00014 at *E/N* = 162 Td, while the ratio of the ion intensity of O_2^+ (*m/z* 32) to that of H_3O^+ was 0.02–0.03. The ion count rates of the product ions totaled (4–16) × 10^2 ncps normalized to an H_3O^+ intensity of 10^6 cps, which is within the linear dynamic range of the PTR-MS instrument.

The stated purities of gases and chemicals used were as follows: air, >99.99995% (Japan Fine Products); methanol/N_2, 10.8 parts per million (ppm) (Takachiho); ethanol/N_2, 9.56 ppm (Takachiho); 2-propanol ($(CH_3)_2CHOH$)/N_2, 10.55 parts per million (ppm) (Sumitomo Seika Chemicals); ethanol, >99.5% (C_2H_5OH; Kanto Kagaku); ethyl–2,2,2–d_3 alcohol, 99 atom % D (CD_3CH_2OH; Isotec); ethyl–1,1–d_2 alcohol, 98 atom % D (CH_3CD_2OH; Isotec); isopropyl–

1,1,1,3,3,3–d_6 alcohol, 99.8 atom % D ($(CD_3)_2CHOH$; C/D/N isotopes); isopropyl–2–d_1 alcohol, 99.4 atom % D ($(CH_3)_2CDOH$; C/D/N isotopes); acetic acid, >99.99% (Sigma-Aldrich); and acetic 2,2,2–d_3 acid, 99.5 atom % D ($CD_3C(O)OH$; C/D/N isotopes).

Results and Discussion

Figure 1(a) shows the ion signals of protonated ethanol, $C_2H_5OH{\bullet}H^+$, at *m/z* 47 (M47) and of H_2DO^+ at *m/z* 20 (M20) before and after the introduction of the C_2H_5OH sample at *E/N* = 108 Td. As expected, the ion signals of the protonated ethanol increased with ethanol as the sample gas, while the ion signals at *m/z* 20 did not change. The background ion signals at *m/z* 20 were relatively high because of the ion signals from H_2DO^+ and $H_3{}^{17}O^+$, which intensities are 0.015 % and 0.038 % of that of H_3O^+, respectively. Figures 1(b) and 1(c) show results from the same experiments, but with CD_3CH_2OH and CH_3CD_2OH, respectively. In both cases, enhancement of the ion signals at *m/z* 20 (M20) was observed, as well as an increase of the ion signals of protonated ethanols at *m/z* 50 for CD_3CH_2OH (M50) and *m/z* 49 for CH_3CD_2OH (M49), respectively. Previously, we reported that the extent of an H/D exchange between H_3O^+ and ethylbenzene–d_{10} was too small to be observed by PTR-MS. Similarly, the formation of H_2DO^+ is unlikely to result from the H/D exchange between H_3O^+ and deuterium-labeled ethanols, but instead results from the reaction of H_3O^+ with deuterium-labeled ethanols:

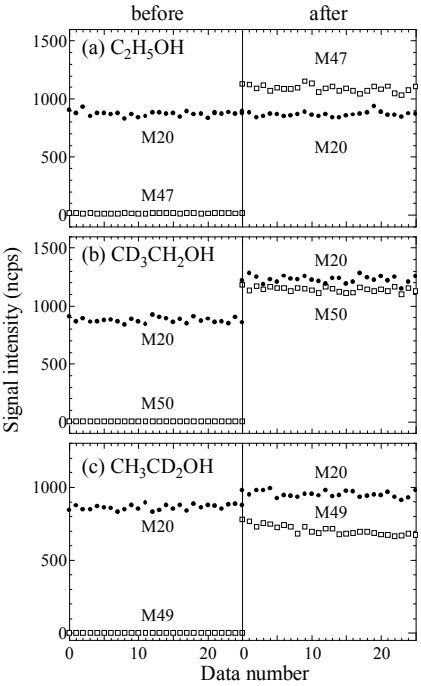

Figure 1. Differences in the ion signals of protonated ethanol and H_2DO^+ before and after the introduction of ethanols at E/N = 108 Td. (a) C_2H_5OH, (b) CD_3CH_2OH, and (c) CH_3CD_2OH.

$$H_3O^+ + CD_3CH_2OH \rightarrow C_2H_2D_2 + H_2DO^+ + H_2O \quad (4)$$

$$H_3O^+ + CH_3CD_2OH \rightarrow C_2H_3D + H_2DO^+ + H_2O \quad (5)$$

The experimental detection sensitivity obtained from count rates for protonated ethanol, $C_2H_5^+$, CH_2OH^+, and reproduced H_3O^+ was compared with the value calculated from the reported rate constant for the reaction of H_3O^+ with ethanol. However, approximately 80 % of the overall H_3O^+ + ethanol reaction was unidentified. The branching ratio for channel reproducing H_3O^+ is possibly underestimated owing to loss processes of H_2DO^+ ions. Therefore, the unidentified channel was probably the channel that re-produced H_3O^+ ion. The reproduction of the H_3O^+ ions was found to be significant in the detection of ethanol by PTR-MS.[1]

Figure 2(a) shows the ion signal of a fragment ion, $(CD_3)_2CH^+$, at *m/z* 49 (M49) and the ion signal of H_2DO^+ at *m/z* 20 (M20) before and after the introduction of the $(CD_3)_2CHOH$ sample at *E/N* = 139 Td. After the sample was introduced, not only did the ion signals of $(CD_3)_2CH^+$ increase, but the ion signal at *m/z* 20 (M20) also increased, from 887 ± 81 ncps to 1260 ± 93 ncps.

$$H_3O^+ + (CD_3)_2CHOH \rightarrow H_2DO^+ + CD_2CHCD_3 + H_2O \quad (6)$$

Similarly, the ion signals of the fragment ion $(CH_3)_2CD^+$ at *m/z* 44 (M44) and of H_2DO^+ at *m/z* 20 (M20) before and after the introduction of the $(CH_3)_2CDOH$ sample at *E/N* = 139 Td are shown in Fig. 2(b). The ion signal of $(CH_3)_2CD^+$ increased after the addition of the sample gas, while a slight increase in the ion signal at *m/z* 20 was observed: 873 ± 71 ncps before compared to 933 ± 99 ncps after:

$$H_3O^+ + (CH_3)_2CDOH \rightarrow H_2DO^+ + C_3H_6 + H_2O \quad (7)$$

In contrast to the reaction of the deuterium-labeled 2-propanols, the reaction of H_3O^+ with $CD_3C(O)OH$ did not produce H_2DO^+ even at *E/N* = 139 Td (875 ± 99 ncps before compared to 877 ± 84 ncps after), as shown in Fig. 2(c). The ion signals of the protonated $CD_3C(O)OH$ at *m/z* 64 (M64) increased after the introduction of the $CD_3C(O)OH$ sample. The absence of the channel reproducing H_3O^+ was confirmed for reaction. The detection sensitivity for acetic acid was in good agreement with the sensitivities calculated from the experimentally and theoretically obtained rate constants for the reaction of H_3O^+ with acetic acid.

On the other hand, the detection sensitivity for 2-propanol were quite small compared with the calculated values. The difference the difference between the experimental and calculated detection sensitivities for 2-propanol was attributed to the reaction channel that re-produced H_3O^+ ion during the reaction of H_3O^+ with 2-propanol.[2]

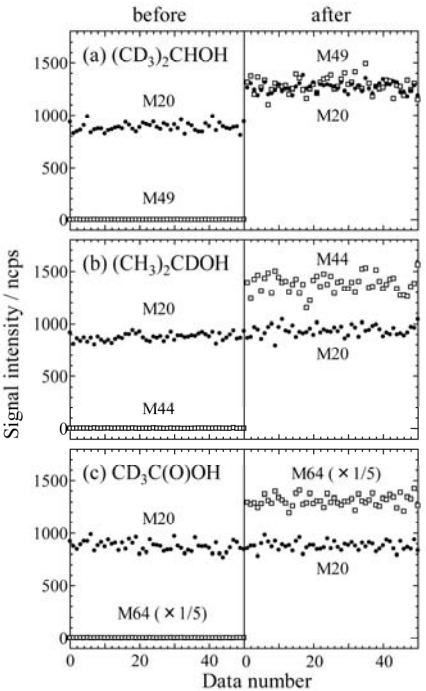

Figure 2. Ion signals of propyl radical ions and H_2DO^+ before and after the introduction of (a) $(CD_3)_2CHOH$ and (b) $(CH_3)_2CDOH$ at E/N = 139 Td; (c) ion signals of protonated acetic acid and H_2DO^+ before and after the introduction of

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Field chamber studies on nucleation potential of the ambient air

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Introduction

We studied secondary particle formation using a Teflon chamber in field conditions. The chamber was placed in boreal forest and filled with particle free air. Only the same condensational gases as in the atmosphere entered the chamber. Under right conditions these gases started nucleating inside the chamber when the chamber was closed. The secondary particle formation in chamber was studied by measuring both the particle and the gas phase. The gas composition measurements give information about the gases participating in the new particle formation (NPF). The particle phase measurements aimed to characterize NPF events and compare the events detected inside the chamber to the particle formation events observed in the atmosphere. This field study gives insight into which gases participate to the secondary particle formation and the condensational growth of these particles.

Methods

The chamber studies were carried out between July and August 2010 at the SMEAR II station in Hyytiälä, Southern Finland. The chamber is a 10.6 m long cylinder with a radius of 1.16 m (volume 44.8 m3) and it is made of FEP Teflon film [1]. The new particle formation inside the chamber was observed with Differential Mobility Particle Sizer (DMPS) and Condensational Particle Counters (CPC). Those measured the number size distribution of the secondary particles in size range 10-450 nm and the total concentration of particles larger than 3 and 10 nm. The composition of the gas phase in the chamber was measured with the Proton Transfer Reaction Mass Spectrometer (PTR-MS), Chemical Ionization Mass Spectrometer (CIMS) and O_3-, NO-, NO_x-, and SO_2 gas analyzers. Additionally an online gas chromatograph/mass spectrometer was used to identify the organic gas compound species. The comprehensive particle and gas phase measurements at SMEAR II site provided information on simultaneous atmospheric conditions**.**

Conclusions

The aim of this study was to investigate the nucleation potential of the boreal air masses. The nucleation experiments were performed inside the cylindrical Teflon chamber, which was filled with particle free air containing only the atmospheric gases. New particle formation and subsequent growth were detected on almost every experiment when the background particles

were removed. The number concentration of the newly formed particles varied between 10000-27000 cm^{-3}. The radiation seemed to limit nucleation inside the chamber; on rainy and overcast days (when only diffuse radiation present) NPF events were typically not observed. Median growth rate for nucleation mode particles were calculated to be 12.1±0.2 nm/h. This value is much larger than growth rates typically measured in the atmosphere in Hyytiälä, 1-6 nm/h [2]. Small condensation sink and absence of the Aitken mode background particles explains partly the observed fast growth rates. During the particle formation inside the chamber the condensation sinks were $3.0\pm4.2 \cdot 10^{-4}$ s^{-1}. The CSs observed inside the chamber are about an order of magnitude smaller than the ones observed in atmosphere in Hyytiälä during NPF events.

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Intercomparison of PTR-MS and PTR-TOF-MS measurements during the BEACHON ROCS field campaign

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Abstract

The BEACHON (Biosphere-hydrosphere-atmosphere-interactions of Energy, Aerosols, Carbon, H2O, Organics and Nitrogen) long term research initiative was established to shed light on sources, sinks and the atmospheric fate of organic aerosol and precursor gases. The study in August 2010, BEACHON-Rocky mountain Organic Carbon Study (BEACHON-ROCS) focused on the biosphere-atmosphere exchange of reactive organic gases. Here we present first results from this field campaign comparing concentration and flux data of selected volatile organic compounds (VOCs) measured by a PTR-MS and a PTR-TOF-MS instrument. We compare VOC concentrations and fluxes calculated by the disjunct eddy covariance and eddy covariance method. Different data processing methods for analyzing 10 Hz PTR-TOF-MS measurements are evaluated.

Introduction

Volatile organic compounds play an important role in tropospheric ozone chemistry and aerosol formation and can therefore be an important influence on local and global climate [1]. The amount and the chemical species emitted are dependent on the plant species, the age and the health of the vegetation but also on ambient parameters such as temperature, moisture and light levels [2,3,4]. Due to their influence on aerosols and cloud condensation nuclei, biogenic VOCs (BVOCs) are expected to influence precipitation and radiation.

Missing OH reactivity inferred from OH reactivity measurements [5] has led to the assumption that a substantial amount of BVOCs are currently not identified by state of the art analytical techniques. The capability of the PTR-TOF-MS to ionize, detect and quantify a broad variety of VOCs at sampling rates of 10 Hz can be used to address the issue of the presence of unidentified VOCs and whether they are being emitted or deposited. One goal of the BEACHON research project is to elucidate sources, reactivity and fate of the major BVOCs and their oxidation

products. The PTR-TOF-MS is used to help identify new species and measure fluxes to track the fate of volatile organic species.

Experimental Methods

Field Site

The BEACHON ROCS study was located at the Manitou Forest Observatory (MFO) near Woodland Park, Colorado (2300m elev., lat. 39°6'0'' N, long. 105°5'30'' W). MFO is within the U.S. Forest Service Manitou Experimental Forest which is part of a larger zone that extends from Northern New Mexico to Southern Wyoming and is a component of the dominant Western U.S. ponderosa pine forest type that extends from Mexico to Canada. The site is representative of the semi-arid Western U.S. where biosphere-atmosphere exchange processes of energy, water, carbon and nitrogen are particularly sensitive to changes in the precipitation. The site is located in a relatively flat valley with a reasonable upwind fetch, a topography that is amenable to performing flux measurements using micrometeorological techniques. The canopy is open and of varying density, with mixed-age ponderosa pine up to 100 years old and a surface cover of grasses, sage, crocus, forbs and exposed cryptogrammic solids. The Leaf Area Index (LAI) of the pine trees is 2.9 with a canopy cover fraction of 0.66 around the tower resulting in an area average LAI of 1.9.

Instruments

The research site is equipped with meteorological instruments and several instruments measuring VOC concentrations, VOC gradients and VOC fluxes were located at the field site during the field campaign. This study compares data taken by a PTR-MS and a PTR-TOF-MS during the same measurement period in August 2010. The chemistry tower was equipped with a sonic anemometer and Teflon inlet lines at several heights.

The PTR-MS sampled sequentially from six gradient lines (1/4" OD; heights at 1, 3.5, 7, 10, 15.5 and 23 m) and a separate 3/8" line (eddy covariance line; height at 18 m) dedicated to flux measurements, where a fast response time was required. The delay time measured through the eddy covariance line was on the order of 3-5 seconds; it was about 20 seconds through the gradient lines. The sampling sequence of the PTR-MS was as following: VOC gradients were measured for 120 minutes, where each level was sampled for 5 minutes to obtain a full profile every 30 minutes. Every 120 minutes a valve was switched and fluxes of a selected set of VOCs (MBO and monoterpenes) were measured by DEC for 30 minutes. Background measurements through a catalytic converter were performed every 4 hours for 5 minutes.

The PTR-TOF-MS sampled continuously from the same eddy covariance line as the PTR-MS. The 10 Hz data were saved in 6 min files (hdf5 file format (http://www.hdfgroup.org)) using the TOF-DAQ v1.72 software (Tofwerk AG, Switzerland). A description of the instrument and the data acquisition are given at [6,7,8]. The data post processing was done by Matlab (Mathworks, USA) functions described by [8], to obtain mass scale spectra between m/z 17 to m/z 315. Mass scale calibration was done by continuously adding dichlorobenzene (protonated m/z 180.9373) and trichlorobenzene (protonated m/z= 146.9763) into the PTR-TOF inlet. Background measurements through a catalytic converter were performed every 7 hours for 25 minutes.

Results and Discussion

First results from the BEACHON ROCS field campaign in August 2010 are shown with a main focus on comparing the two different PTR-MS systems. VOC concentrations are intercompared between the top gradient line for PTRMS and the Eddy covariance (EC) line for the PTR-TOF-

MS. MBO and monoterpene concentrations and fluxes are also compared when both instruments sampled from the EC sampling line. Fluxes of the masses measured by PTR-MS are calculated by the disjunct Eddy covariance method. Fluxes of the data measured by PTR-TOF-MS (10 Hz) are calculated by the Eddy covariance method. The concentration intercomparison is done for methanol, acetonitrile, acetaldehyde, acetone, MBO and monoterpenes. The flux intercomparison is focused on monoterpenes and MBO. Additionally a 5 day period was picked to compare different 10Hz PTR-TOF-MS data processing techniques developed over the last years.

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Flavour release using mass spectrometry: PTR-ToF versus APCI-ion trap.

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Abstract

Flavour release, either in vitro (headspace) or in vivo (nosespace), is advantageously studied by mass spectrometry using atmospheric pressure ionization like proton transfer reaction (PTR) or atmospheric pressure chemical ionization (APCI).

The results obtained with a new time-of-flight (ToF) instrument equipped with a PTR source [1] have been compared to those obtained with an ion trap mass spectrometer equipped with an APCI source developed in Dijon [2]. Headspace analyses of aqueous solutions of various flavour molecules varying in terms of hydrophobicity (log P), volatility and chemical class [acetic acid, butyric acid, acetoine, diacetyle, 3-methylbutanal, 3-methylbutan-1-ol, ethyl hexanoate, heptan-2-ol, 2,3,5-trimethylpyrazine, γ-decalactone] have been performed on both instruments. These instruments have been compared in terms of response factor, linearity and limit of detection.

Both instruments displayed similar results, particularly for the limits of detection and linearity range. The PTR-ToF instrument displayed faster and more reliable responses for hydrophilic molecules. Despite the tandem MS capabilities of the ion-trap instrument, a clear advantage of the ToF one is the separation of isobaric species [for example: m/z 87.044 for diacetyle versus m/z 87.080 for 3-methylbutanal or m/z 89.059 for acetoine versus 89.096 for 3-methylbutan-1-ol] allowing easier distinction of compounds in complex mixtures of flavours.

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Estimation of Mass Transfer Coefficients of Volatile Sulfur Compounds in Biofilters Measured by Proton-Transfer-Reaction Mass Spectrometry

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Abstract

Biofiltration has been suggested as a cost-effective technique for treating malodorous emissions from livestock facilities. The efficiency has been suggested to be mainly limited by insufficient mass transfer of volatile sulfur compounds from air to the liquid phase. A better understanding of limitations of the mass transfer process is therefore important in order to enhance the performance and design of biofilters. In this study, a method based on Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) has been developed in combination with a developed computer model to estimate the mass transfer coefficients in biofilters for selected packing materials and volatile sulfur compounds. PTR-MS was used to provide profiles of injected sulfur compounds with adequate sensitivity, time resolution and reproducibility. Different injection strategies were used and compared to each other in order to optimize the method. Measured profiles from inlets and outlets of biofilters were modeled using the advection-dispersion equation modified for mass transfer between mobile and immobile gas phase. 2-butene was chosen as a conservative tracer gas for estimation of diffusion-dispersion coefficients and mobile air contents due to its low solubility in water and detectability by PTR-MS. Mobile-immobile mass transfer coefficients were estimated by fitting of measured profiles of sulfur compounds individually. Toluene was used as a reference compound for validation of the method and comparison of mass transfer coefficients from literatures. The study demonstrates the possibility for estimating compound specific mass transfer coefficients for biofilter materials using PTR-MS in combination with computer modeling.

Breath gas analysis by PTR-TOF-MS in a clinical setting

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Abstract

Typical clinical (breath analysis) studies take several months to years. Employing a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) as an analytical tool for breath analysis, a constant performance of the instrument is essential. Here we report on the long-term performance of a PTR-TOF-MS for the analysis of exhaled breath gas in the frame of a clinical study. Performance data are shown for a period of 7 months. We characterized the sampling procedure, sample storage, and measured sensitivity and detection limit for a set of VOCs with relevance in breath analysis. Over the period of 7 months, we were able to achieve a high mass accuracy and precision in the range of ppm.

Air-sea exchange of volatile organic compounds - Wind-wave canal measurements

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Abstract

Air – sea gas exchange is of critical importance to the chemistry and physics of the lower atmosphere; as a consequence there is a great need for understanding the mechanisms controlling the gas transfer between ocean and atmosphere. This study focuses on measuring the exchange transfer velocities for a number of key volatile organic compounds (VOCs), as a function of wind speed (e.g. DMS, acetone, methanol, isoprene). To access the gas exchange mechanisms we simulated the ocean - atmosphere interactions in the "Aeolotron" wind wave facility in Heidelberg. A range of low and high soluble VOCs were introduced to the 10 m diameter ring-form chamber containing circa 21500 m3 water and the wind speed varied by the use of ceiling mounted turbines. Low soluble species such as DMS were introduced into the liquid phase and more soluble species such as acetone into the gas phase. Proton Transfer Reaction Mass Spectrometer (PTR-MS) equipped with a quadruple mass spectrometer was used to follow small changes in the gas phase tracer concentration during the exchange. The calculated transfer velocities will be used to compare with current estimates where available, and the effect of new or altered transfer coefficients will be assessed with state-of-the-art global models. Furthermore by integrating the PTR-MS measurements with results from other instruments (e.g. wave surface topography, FTIR-Spectroscopy) we aim to elucidate the fundamental physical mechanisms of air sea transfer. These results will lead to a better understanding of the individual VOC global budgets and thereby improve predictions of future atmospheric composition and responses to climate change.

PTR-TOF / HT-PTR-MS studies on amines and their atmospheric degradation products

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Abstract

Carbon dioxide (CO_2) can be captured from the flue gas of coal- or gas-fired power stations using amine-based scrubber solutions. Amine slip to the atmosphere may, however, lead to the formation of substances that are harmful to humans and the environment. The overall objective of the ongoing University-of-Oslo led project "Atmospheric Degradation of Amines" (ADA) (http://ada.nilu.no/) is to contribute to the understanding of the atmospheric degradation of amines emitted to the atmosphere from CO_2-capture plants. Specific objectives are to identify and quantify the gas- and particulate phase photochemical degradation products. To achieve these objectives we performed a series of smog chamber experiments in the European Photoreactor (EUPHORE) in Spain and in the Innsbruck photoreactor. We used a PTR-TOF 8000 instrument and a High-Temperature PTR-MS instrument for on-line analysis of amines and amine photo-oxidation products (amides, nitrosamines, nitramines and imines), both in the gas and particulate phase. Here, we will focus on the analytical aspects of our work and present results on method development and validation.

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BVOCs observation in a warm-temperate deciduous broad leaved forest

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Abstract

Many kinds of trees, fungi and bacteria emit biogenic volatile organic compounds (BVOCs) in the forest. Emission inventories show that isoprenoid is the most prominent compound of BVOC. The amount of carbon emitted by plants as isoprene (C_5H_8), which is probably the most substantial fraction of isoprenoid emission, accounts for up to 2% of NPP in most cases, but can reach higher values (15-50%) under special conditions. The emission of BVOCs contributes significantly to the reactive hydrocarbons and net carbon budget in the troposphere and greatly influences atmospheric chemistry through the region-wide formation of photochemical oxidants and the lifetime of methane. Thus, precise measurement of the BVOCs flux of forests is needed. However, the characteristics and mechanisms of BVOCs flux have not been sufficiently evaluated in forests, mainly due to the difficulty of continuously measuring the BVOCs flux. To evaluate mechanisms of BVOCs flux, the measurement system should measure the flux on soil, leaf and above the canopy at the same time. Therefore, we developed an observation system for continuously measuring the BVOCs flux for forests and conducted preliminarily flux measurements using Proton Transfer Reaction Mass Spectrometry (PTR-MS) in Yamashiro Experimental Forest (YEF). YEF is located in a valley in a mountainous region of western Japan (Kidugawa City, Kyoto Prefecture; 34°47'N, 135°50'E; 220 m a.s.l.). The hillslope between the ridge top and the valley bottom is steep (about 30°), but the slope of the main river channel is gentle (about 5°). The valley is underlain by weathered granite, and the soil is generally thin, immature, and sandy. The annual mean temperature was 15.5°C, and the hourly maximum and minimum temperatures in August and January that year were 34.8°C and 3.9°C, respectively. Annual mean precipitation was 1449 mm; the rainy season was from late June through early July, and typhoons occurred during the summer and fall. The forest consists of more than 50 deciduous (mainly *Quercus serrata Thunb* ex. Murray) and evergreen (mainly *Ilex pedunculosa* Miq) broadleaf species. The forest canopy is closed, and the canopy height is about 12 m on average. In the present study, we measured BVOCs emission rate from soil and branch of *Q. serrata* using the automated multi closed chamber method. We also measured forest level flux using the Relaxed Eddy Accumulate (REA) method. Clear positive isoprene flux were observed at around noon using the REA and branch chamber method. Those patterns of daily change were corresponding including the time of a small temporary decrease. On the other hand, isoprene emission was not observed on soil. Isoprene emission from *Q. serrata* was strongly dependent on leaf temperature. The observation of the surface temperature on canopy using the thermography might be effective for the accurate estimation of forest level isoprene flux.

Total OH reactivity measurements above and within the Boreal forest – HUMPPA 2010

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Abstract

The Boreal forest covers a large area on earth, comparable in size to the Tropical rain forest, and has a significant impact on the regional atmospheric chemistry and physics. Here we present measurements of total OH reactivity using a PTR-MS from a Finnish Boreal forest station in Hyytiälä (Latitude 61° 51' N; Longitude 24° 17' E) between July and August 2010. The total OH reactivity measurement is a direct, in-situ determination of the total loss rate of OH radicals (in sec^{-1}) caused by all species in ambient air. During this campaign (HUMPPA 2010) for the first time the OH reactivity has been measured both inside and directly above the canopy using the recently developed comparative reactivity method described by Sinha et al. 2008. The predominately coniferous forest vegetation is known to emit significant amounts of biogenic volatile organic compounds, such as monoterpenes, sesquiterpenes, methanol and acetone. By comparing the OH reactivity contribution from individually measured compounds and the directly measured total OH reactivity, the size of any unaccounted for or "missing" sink can be deduced. The impact of various local and regional influences on total OH reactivity such as temperature dependent biogenic emissions, biomass burning plumes and a nearby sawmill will be shown. The vertical gradient of OH reactivity through the canopy will be discussed in terms of photochemistry.

Variation of VOC volume mixing ratios in high latitude urban and rural location

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Abstract

VOC volume mixing ratios were measured at high latitude urban measurement station SMEAR III in Helsinki and rural measurement station SMEAR II in Hyytiälä both in Southern Finland. In this study we compared variations of biogenic and anthropogenic VOC volume mixing ratios (VMRs) at these two measurement stations during a winter and a spring period.

Introduction

In global scale biogenic VOC emissions are estimated an order of magnitude higher than anthropogenic ones. Even in Europe there are countries in which biogenic emissions surpass anthropogenic ones (1). In Finland the biogenic emissions are estimated to be two times higher than anthropogenic ones (2) on an the annual level. However, on temporal and spatial scale the emissions have large variation: anthropogenic emissions are dominated by point and line sources such as power plants and roads in urban areas, while biogenic emissions come from larger areas covered by vegetation and the emissions are lowest in winters when the biogenic activity is low.

We conducted online measurements of ambient VOC VMRs in an urban and rural location in Finland during a winter and a spring period. Using this data we were able to study VOC VMRs diurnal behavior and their seasonal changes in these two different sites. In this study we describe differences of various VOC VMRs in the urban and rural air during mid winter and onset of biogenic activity in the spring.

Experimental Methods

Ambient VOC VMRs were measured with a PTR-MS at urban SMEAR III (Station for measuring Ecosystem-Atmosphere Relations III) in Helsinki (60°15´N, 25°03´E, 26 m above sea level (a.s.l.). The SMEAR III is a measurement site located 5 kilometers northeast from the downtown of Helsinki where trace gases, aerosol particles and urban micrometeorology are studied (3,4). The surrounding of the measurements station is heterogeneous. In the vicinity of the measurement station there are both vegetated areas and major roads. In this study we concentrate on two time periods: 11.-18.1.2006 called urban winter and 26.4-2.5.2006 called urban spring. Ambient air VMR measurements were done in fourth floor of a five storey building. Sample air was pulled through few meters of Teflon tubing from outside the building into the PTR-MS.

The other site where VOCs were measured is rural SMEAR II located in Hyytiälä (61°51´N, 24°17´E, 180 m a.s.l.) 220 km north from Helsinki. At this site there are continuous long term measurements of aerosol particles and micrometeorology (5). We have chosen a rural winter (14.1-20.1.2007) and rural spring (26.4-2.5.2007) similar to the urban measurement periods at the SMEAR III. At the rural SMEAR II the VMRs of the VOCs were measured with a PTR-MS from 14 m height inside the forest canopy. The SMEAR II measurement set up, calibration procedure

as well as the volume mixing ratio calculations used for all VOC data are presented earlier in detail (6).

Results and discussion

At the urban location the compounds originating from the traffic sources have a distinct diurnal cycle (figure 1) whereas at the rural location the VMR changes little during the day (figure 2). Toluene (M93) has a very clear diurnal cycle in both winter and spring in Kumpula. Benzene (M79) has both morning and afternoon rush hour peaks in the urban winter but the afternoon peak is clearer. In the urban spring benzene has a clear peak in the morning.

The typical diurnal cycle of monoterpenes (M137) at the urban site has a maximum during the morning and the afternoon and a minimum in the night (figure 1). Especially in the urban winter peaks can be seen in the morning and in the afternoon. In the urban spring monoterpenes have clearer peak at morning than urban winter. In the urban site the diurnal cycles of benzene and monoterpene are similar. In the rural site monoterpenes have high VMRs in the early morning and in the evening (figure 2).

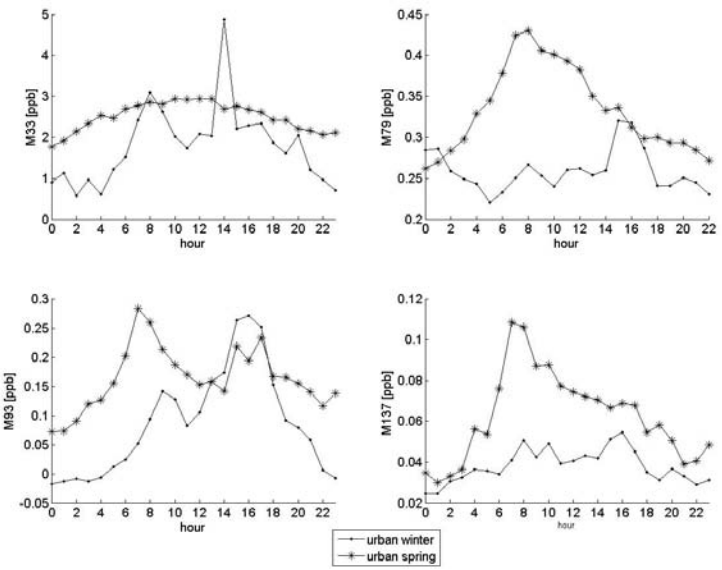

Figure 1: Winter and spring time diural variations for selected VOCs in urban site Kumpula. M33: methanol, M79: benzene, M93: toluene, M137: monoterpenes.

Diurnal behaviour of monoterpenes in the urban site SMEAR III seems to be opposite to the typical diurnal cycle at the rural remote areas with coniferous forest cover (7, 8).

Methanol (M33) seems to have pronounced diurnal behaviour in both the urban winter and the urban spring. In the urban winter there are a few peaks during the morning and the afternoon which may be caused by the traffic. In the urban spring ascending volume mixing ratios can be influenced by biogenic effect. When comparing the diurnal cycles of methanol at the urban and rural sites it can be seen that in the rural winter VMR is quite constant during the day. In the rural spring VMR is higher than in the winter and it has some kind of diurnal variation (Figure 2) likely due to the biogenic effect.

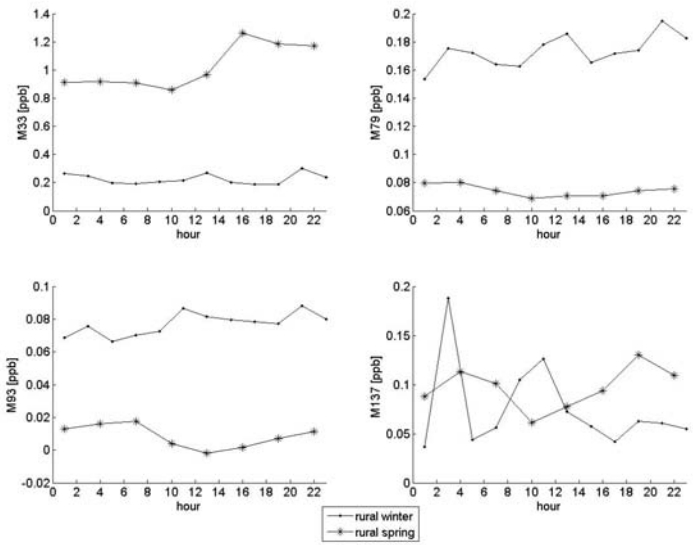

Figure 2: Winter and spring time diural variations for selected VOCs in rural site Hyytiälä. M33: methanol, M79: benzene, M93: toluene, M137: monoterpenes.

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Detection of Explosives Using PTR-TOF-MS

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Abstract

The recent development of proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) has already proven to be extremely valuable in many scientific areas such as detection of illicit substances [1-4], food science [5-6], atmospheric/environmental science [7] and breath gas analysis [8]. In this study, a PTR-TOF 8000 instrument (Ionicon Analytik GmbH) was used in order to detect explosive compounds by the direct sampling of the headspace above small solid quantities (approximately 50 mg) of the explosives placed in glass vials at room temperature, i.e. with no heating or pre-treatment of the sample. The very high mass resolution (m/Δm of 8000) of the PTR-TOF 8000 instrument implies that a high level of confidence can be placed on the detection of explosives and other compounds.

Introduction

The deployment of a time-of-flight detector instead of a quadrupole in a PTR-MS instrument has shown to exhibit major benefit in many areas of research. Due to the high mass resolution compounds with the same nominal mass but different chemical composition are detected at different m/z which greatly helps in identification of compounds [4]. Due to the high time resolution full mass spectra can be recorded in split seconds making direct eddy covariance measurements possible [7]. No pre-selection of ions is needed implying that full mass spectra can be obtained thus making it possible to monitor hundreds of compounds simultaneously, which, for example, greatly aids in elucidating time dependent atmospheric chemistry processes and ion-molecular reactions [3, 7]. Another important benefit is the increased transmission of high m/z ions in TOF compared to quad [9].

We have previously shown the capabilities of PTR-TOF-MS in detection of illicit substances, such as explosives [1, 2], chemical warfare agent simulants [3] and drugs [4]. Measurement of a few of these compounds is problematic due to their associated low vapor pressures but, nevertheless, the protonated parent molecule could always be detected thus providing a high level of confidence in their detection. For several compounds dissociative proton transfer occurred to various degrees; for other compounds taggants and impurities were found, and for a few compounds more unusual E/N dependencies were discovered. As will be described here all of these effects, in conjunction with the high mass resolution of the PTR-TOF 8000, help in identifying an illicit compound to a very high level of confidence in real time.

Experimental Methods

A PTR-TOF 8000 instrument (Ionicon Analytik GmbH) was used in order to conduct the measurement reported here. A detailed description of this instrument can be found elsewhere [9]. The experimental details are very similar to our recently reported measurements of explosives [1, 2], chemical warfare agent simulants [3] and illicit drugs [4]. A small piece of the sample (approx 50 mg) was placed in a vial (without any sample pretreatment) kept at room temperature and the headspace was measured at a drift tube pressure of 2.3 mbar and a drift tube temperature of 90 °C. The measurement was recorded over a large E/N range (approx 80-200 Td) by changing the drift tube voltage.

Results and Discussion

Figure 1 displays as an example the results from measurement of trinitrobenzene ($C_6H_3N_3O_6$, exact protonated mass of 214.010) at 130 Td. The protonated parent molecule is detected at m/z 214.01. The full mass spectra revealed two impurities in the sample; dinitrobenzene ($C_6H_4N_2O_4$, protonated mass of 169.025 and dinitroaniline ($C_6H_5N_3O_4$, protonated mass of 184.036). At a first glance a possible product following dissociative proton transfer of trinitrobenzene could be loss of NO to produce $C_6H_3N_2O_5$ (exact mass of 184.012). This fragment can though be rejected in favor of dinitroaniline since the m/z measured was 184.035 (see insert in Fig. 1) showing the importance of the high mass resolution. Dinitroaniline has previously been detected as an impurity in trinitrobenzene samples [10].

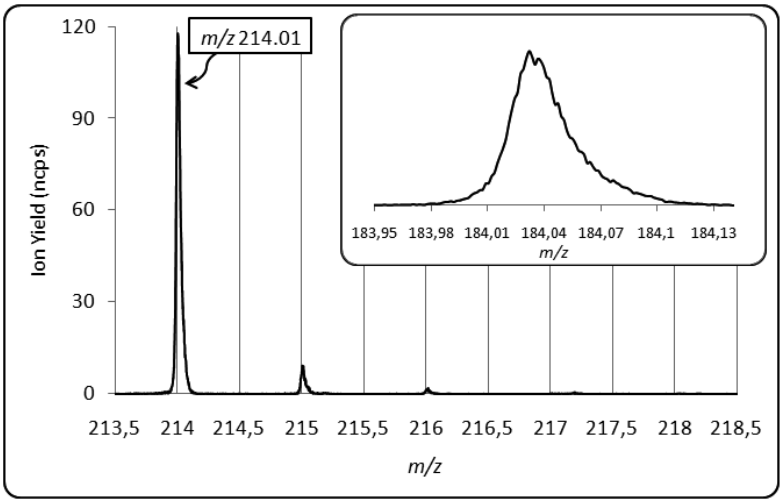

Figure 1: Mass spectra of a sample of trinitrobenzene showing protonated trinitrobenzene at m/z 214.01 and its isotopic peaks at m/z 216.015 and m/z 217.015. The insert shows protonated dinitroaniline at m/z 184.035 from the same measurement file.

Acknowledgment

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CAM and PW wish to acknowledge the EPSRC (EP/E027571/1) that in part supported this work. FP and SJ acknowledge the support of the Community under a Marie Curie Industry-Academia Partnership and Pathways (Grant Agreement Number 218065).

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On-line monitoring of root-induced volatiles in Brassica nigra plants infested with Delia radicum L. root fly larvae

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Abstract

Plants emit different volatile organic compounds (VOCs) upon herbivore attack. These VOC emissions often show temporal dynamics which may influence the behavior of natural enemies using these volatiles as cues. This study analyzes on-line VOC emissions by roots of *Brassica nigra* plants under attack of cabbage root fly larvae, *Delia radicum.* Root emitted VOCs were analyzed with a combination of Proton-Transfer Reaction Mass Spectrometry (PTR-MS) and Gas Chromatography Mass Spectrometry (GC-MS). Our analyses showed that several sulfur containing compounds, such as methanethiol, dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS) and glucosinolate breakdown products, thiocyanates (TC) and isothiocycanates (ITC) were emitted by the roots in response to infestation. The emissions were subdivided in rapid responses, emerging within hours after infestation, and later responses, evolving only after 12 hours. The most typical marker for rapid responses was mass 60. We identified m60 as thiocyanic acid (HCNS), which is also a prominent fragment of TC or ITC spectra. The emission of m60 stopped when larvae had pupated, which makes it an excellent indicator for actively feeding larvae. Methanethiol, DMS and DMDS levels increased much later in infested roots, indicating that activation of enzymes and genes involved in the production of these compounds is needed. Both the early and late responses can play a role in tritrophic interactions associated with *Brassica* species. The identification and dynamic patterns of the responses may help to design non-invasive analytical procedures to assess root infestations.

Henry's Law Constant & Quantitative Structure Property Relationships (QSPR)

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Abstract

Henry's law constant is a basic physico-chemical property and describes partitioning of a solute between water and air. It can be measured by Inert Gas Stripping coupled to PTR-MS, yielding consistent data. These data are the basis for improving QSPR models.

Introduction

Henry's law constant describes the partitioning of a compound between water and air at infinite dilution. It is a fundamental parameter, e.g. Henry's law constant (HLC) can be recalculated to partial molar Gibbs-Energy of solvation and the activity coefficient γ. Air-water partitioning coefficients, and partition coefficients in general, are of tremendous practical importance in diverse fields, e.g. separation processes and techniques such as gas chromatography (Kovats indices) [1], environment [2] or flavor perception [3] and flavor release [4, 5] from food matrices.

Due to the low concentrations of the solute at "infinite dilution", typically less than 0.001-0.01 mole fractions and of several experimental pitfalls, Henry's law constants and partitioning coefficients are difficult to measure. Although a number of techniques exist [6], their applicability depends in particular on the range of Henry's law constants to be determined [6], the matrix and on the characteristics of analytes, and certain properties of the solute. Among the techniques, Inert Gas Stripping is particularly used for low solubility (low HLC in M/atm) values [7], and is considered one of the most reliable methods. Though routinely gas chromatography is employed, the good reproducibility, high sensitivity, and, in particular, high time resolution (online-monitoring) together the wide linear detector range of PTR-MS, render the coupling of PTR-MS to Inert Gas Stripping [8] particularly powerful. Furthermore, this technique has been applied not only to measuring air-water partitioning coefficients, but also to partitioning coefficients for other matrixes, such as ethanol-water [9], and even complex matrices such as coffee [10].

Methods

Experimental techniques

In the dynamic headspace technique, the stripping cell is coupled to a mass spectrometer (a proton transfer mass spectrometer, PTR-MS [11]) for the measurement of the exponential decrease of concentrations in the headspace over time [8]. Measurements were performed with a commercially available PTR-MS from Ionicon Analytik GmbH (Innsbruck, Austria) in the HS (High Sensitivity) version equipped with a quadrupole mass analyzer.

Theoretical models

Partitioning coefficients are the basis for a number of theoretical models that connect the structure of a molecule to its chemical properties or biological activities (Quantitative Structure Property Relationships QSPR and Quantitative Structure Activity Relationships QSAR). They allow for the prediction of physico-chemical properties. Examples of some well-known models are Henrywin (fragment-based group and bond contribution methods) [12], as for instance, implemented in the software Henrywin [12], LSER (Linear Solvation Energy Relationship) [1], and SPARC (fragment and theoretical descriptor based) [13].

Results

We present here experimental results of partitioning coefficients measurements with PTR-MS. Sulfur compounds are notoriously known for their pungent and repulsive smell, yet, at low concentrations, are part of the flavor of some foods, e.g. coffee, wine, cheese [14], yogurt[15] and even enhance taste in wine [16]. In addition, we have performed an evaluation of QSPRs based on PTR-MS data for sulfur compounds (see *Figure 1*).

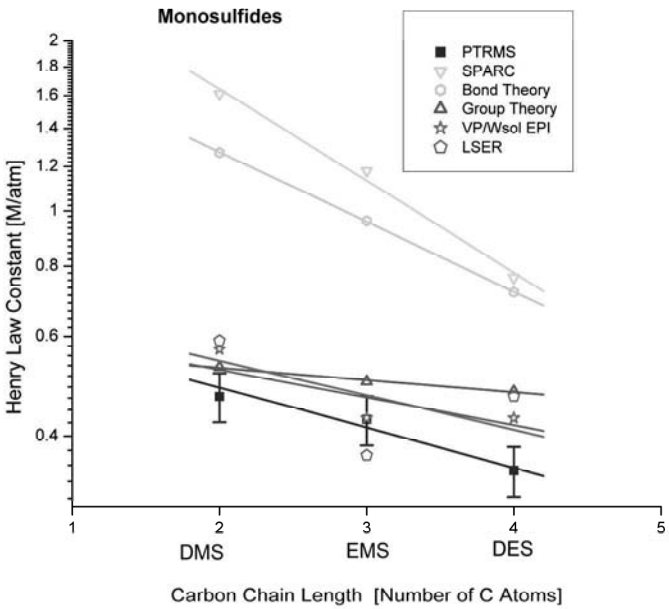

Figure 1: Model evaluation and comparison to PTR-MS experimental data, plotted against the carbon chain length of Sulfides

Discussion

Based on our experimental results and comparison with literature and theoretical modeling we can conclude from the present work that PTR-MS works well for the determination of Henry's law constant. It further allows for the generation of consistent data sets. These data sets are particularly valuable for QSAR development, which often has problems with model verification.

For example, based on our data analysis of models, we recommend the adjustments of models for sulfides and disulfides, in order to yield lower values of HLCs, thus lower values of solubility, and, accordingly, higher values of fugacity.

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Characterisation of a PTR-TOF-MS and its applications in laboratory experiments and field measurements

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Abstract

The Proton Transfer Reaction – Time Of Flight – Mass Spectrometer (PTR-TOF-MS) is a relatively new technique that is applied in laboratory experiments and field measurements for online VOC detection. Therefore the characteristic behaviour of the PTR-TOF-MS under various conditions has to be known.

Our instrument was calibrated using a multicomponent VOC standard and was accordingly characterised for sensitivity, linearity and detection limits. In addition, an intercomparison with a GC-FID was carried out. The PTR-TOF-MS was deployed for measurements of VOC in the urban area of Wuppertal. A significant dependence of the instrument´s sensitivity on ambient temperature was observed during the field measurements. The Instrument was also used for the measurements of secondary VOC formed as a result of the oxidation of substituted aromatic hydrocarbons in simulation chamber experiments. Furthermore, the VOC emissions from the combustion of five different alternative and conventional jet fuels were measured using a pre-mixed burner. Due to the high mass and time resolution the PTR-TOF-MS proved to be a perfect complement to the analytical instruments used previously for these measurements.

Ambient VOCs measurement in winter: Belgrade semi-urban area

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Abstract

In order to assess the ambient levels and possible origin of volatile organic compounds (VOCs), concentrations of thirty one compounds were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) in a semi-urban site of Belgrade. Measurements were conducted in February 2010. One-hour mean values have been calculated and used for further analyze together with meteorological parameters. Unmix receptor model was used to identify the sources of VOCs.

Introduction

As very important local and regional atmospheric pollutants, monitoring of volatile organic compounds (VOCs) and determination of their origin is significant. By affecting OH radical concentrations and the production of photochemical oxidants, VOCs play an important role in tropospheric chemistry. Chemical reactions with nitrogen oxides under sunlight lead to the production of secondary air pollutants, resulting in tropospheric ozone and secondary organic aerosols (SOAs) (Seinfeld and Pandis, 1998). Due to the adverse effects some of them have on human health, monitoring of VOCs in the urban area is very important (WHO, 2000).

VOCs sources in semi-urban areas can be both anthropogenic and biogenic. Major anthropogenic sources include vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions, and industrial processes. Benzene and toluene are compounds associated with traffic emissions, but toluene is also released with the use of solvents (painting, printing, dry cleaning, etc.).

Receptor modeling

Receptor models based on chemical composition have been used intensively for source apportionment. The fundamental principle of receptor modelling is that the mass conversation can be assumed and a mass balance analysis can be used to identify and apportion sources of VOCs. In order to obtain data set for receptor modelling individual chemical measurements can be performed at the receptor site by measuring VOCs concentrations. From a receptor point of view, pollutants can be roughly categorized into three source types: source known, known source tracers (i.e. pollutant is emitted with another well characterized pollutant) and source unknown what lead to main differences between models - the degree of knowledge required about the pollution sources prior to the application of receptor models. For sources that have known tracers but do not have complete emission profiles, factor analysis tools such as Principal Component Analysis (PCA), Unmix and Positive Matrix Factorization (PMF) can be used to identify source tracers. PCA attempts to simplify the description of a system by determining a minimum set of basis vectors that span the data space to be interpreted. The concepts underlying Unmix have already been presented in geometrical and intuitive manner (Henry, 1997) and mathematical details are presented elsewhere (Henry, 2003). In this study, the version of EPA Unmix 6, available from the US Environmental Protection Agency (U.S. EPA, 2007) have been used.

Experimental Methods

VOCs concentrations were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) - Ionicon Analytik, Innsbruck, Austria; which allows real-time measurements in the air with a high sensitivity and a fast time response (Lindinger et al., 1998). The air to be analyzed is continuously pumped through a drift tube reactor where the fraction of VOCs is ionized in proton-transfer reactions with hydronium ions (H_3O^+) - the soft ionization method, that generally does not lead to fragmentation of the product ions what simplifies the interpretation and the quantification of the mass spectra. The mass of the product ion equals the VOC mass plus one atomic mass unit. At the end of the drift tube the reagent and product ions are measured by a quadrupole mass spectrometer combined with secondary electron multiplier detector. The product ion signal is proportional to the VOC mixing ratio. The quantity measured with PTR-MS is usually the intensity of a protonated compound on the mass of which information is obtained what does not directly allow the definite identification of isobars and isomers. The measurements were performed at 6 m above ground, at the platform of the Institute of Physics, ($\varphi = 44^\circ$ 51' N, $\lambda = 20^\circ$ 23' E, Hs = 92 m) Zemun, 10 km northwest of Belgrade centre (Serbia), in the semi-urban area and 100 m far from the right bank of the Danube River. The air was conducted to a PTR-MS system through a 2 m heated Teflon tube (70 ^{0}C), inner diameter 3 mm. The PTR-MS operated at standard conditions with average H_3O^+ ion signal of $3 \cdot 10^6$ cps with less than 2% O_2^+.

Results

PTR-MS was programmed to monitor 31 masses at 100 ms per mass with average measurement cycle was around 4 s. Monoterpenes concentration was estimated as the concentration of ions with protonated mass 137 divided by 0.46, because a certain fractionation of non-oxygenated monoterpenes occurs during ionization in the drift tube resulting in masses 67, 81 and 95. The most abundant was compound with protonated mass m/z 61 (propanole, acetic acid) with mean concentration 23.44 ppbv and peak value of 565.31 ppbv, followed by m/z 33 (methanol) with mean concentration 22.08 ppbv and peak value of 352.96 ppbv, m/z 43 (propylene) with mean concentration 13.39 ppbv and peak value 186.54 ppbv, m/z 45 (acetaldehyde) and m/z 47 (ethanol).

In this study the Unmix model has been used to analyze 1-hour averaged VOCs concentrations during 30 days measurement episode for source apportionment purpose. The analysis generated source profiles and overall percentage source contribution estimates for source categories.

Unmix receptor model was run with 656 observations of 31 input variables. Compounds m/z 54 (acrylonitrile), m/z 63 (dimethyl sulfide) and m/z 87 (C_5 aromatics) had a large signal-to-noise ratio and therefore were excluded because efforts to incorporate more species led to no feasible solution. Five factors were chosen as the optimum number for the Unmix model, details of which are discussed as follows.

Discussion

The first profile extracted by Unmix is the gasoline evaporation related to traffic (unburned vehicle emissions) and, probably, evaporation from gas station situated nearby (about 300 m), having high loadings of compounds with protonated masses m/z 61 (propanol, acetic acid) and m/z 89 (MTBE, 4 dioxane). This source has average contribution of 7%. The second Unmix profile has high loadings of compounds with protonated masses m/z 91 (diethyl sulfide) and m/z 120 (chloroform) and can be interpreted as local solvent use with average contribution of 7%. The third profile extracted by Unmix is the vehicular exhaust having the high loadings of compounds

with protonated masses m/z 93 (toluene), m/z 107 (xylene, C_8aromatics), m/z 121 (C_9aromatics) and medium high loadings of compounds with protonated masses m/z 55 (1.3 butadiene) and m/z 57 (acrolein, butene). Its average contribution is 19%. The forth Unmix profile has high loadings of compounds which can be related to (biomas/ biofuel burning with average contribution of 33%. The fifth Unmix profile has high loadings of compounds which can be interpreted as industrial solvent and painting sources with average contribution of 34%. The identified source time series plots are presented on Figure 1.

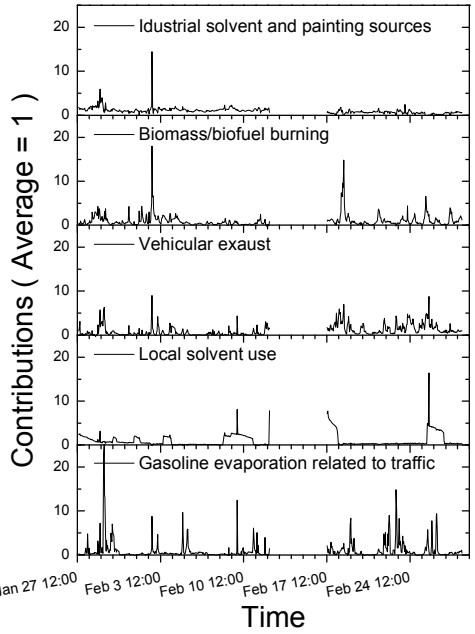

Figure 1: Unmix resolved source contributions time series

Diurnal patterns of source contributions

The average diurnal patterns of source contributions estimated by the two models are shown in Figure 2. The total VOC concentrations were higher in the day than at night since the most sources are related to human daytime activities. The first and third factors were related to traffic and showed typical morning and afternoon rush hours peaks. The second factor associated with solvent use, showed no pronounced peaks during working hours, which may point to constant evaporation from some warehouse. The fourth factor related to biomass/biofuel combustion showed morning peak and in the late afternoon, mostly reflecting traffic density. The maximum was extended late in the evening as a result of the use of various biofuels for individual heating units. The compounds grouped in fifth factor had higher concentrations during daytime.

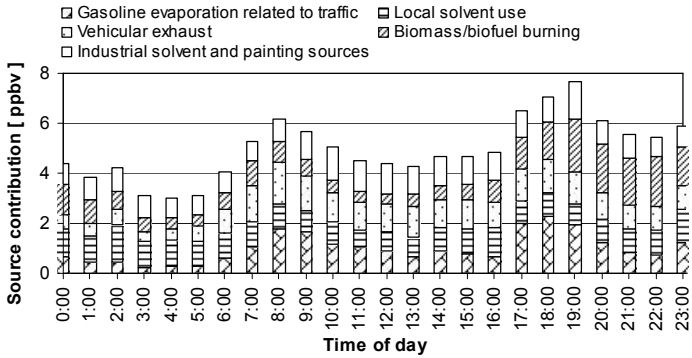

Figure 2: Diurnal patterns of source contributions estimated by Unmix

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Comparison of in situ and filter measurements of organic aerosol at Mt. Sonnblick observatory, Austria

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Abstract

Aerosol (particulate matter) plays an important role in climate change due to significant impact on radiative forcing through the scattering and adsorption of solar radiation. Normally in the atmosphere there are both organic and inorganic aerosol constituents. Organic aerosol makes up ≈50% of total submicron aerosol in the troposphere. Here we performed comparison of two different techniques to measure the chemical composition of organic aerosol: in situ and filter measurements. In situ measurements were performed using hr-TD-PTR-MS technique (high mass resolution thermal desorption proton transfer reaction mass spectrometry)[1]. It is a high precision technique with low detection limit. In this work this technique is considered as reference. Weekly high-volume filter samples were collected between July 16 and August 27, 2009, by colleagues from the Vienna University of Technology. Analysis of the filters was done by stepwise heating of a filter aliquot in an oven and PTR-MS analysis of the evaporating organic compounds. Comparing in situ and filter measurements we want to investigate the reliability of offline PTR-MS filter measurements. In Figure 1 the three main cases of the abovementioned comparison are shown. In the first case (figure 1, a), the in situ signal is higher than filter signal. This is probably due to the loss of semivolatile compounds from the filter samples, namely the ones causing the ion signal detected on mass 59.050 Da ($C_3H_6OH^+$). Alternatively, chemical reactions on the filter (between the time of sampling and analysis) may have changed the chemical composition of the organic aerosol burden in a way that less m59.050 fragments are produced during evaporation and protonation. Second and most common case is presented on figure 1, b (mass 155.072 Da, $C_6H_{10}O_3H^+$). In this case the filter signal is higher than the in situ signal. The most plausible explanation is that the filter samples picked up significant contamination from semivolatile gas phase compounds that condensed on the filters during the one week sampling period and/or during storage. Such contamination is less likely to occur in the in situ measurements because instrumental background and possible contamination from gas phase semivolatile compounds are monitored and corrected for on a regular basis. The third case is when good agreement is observed between in situ and filter measurements (e.g. for mass 46.029 Da, CH_3NOH^+). Upcoming research will focus on the processes causing the observed artifacts.

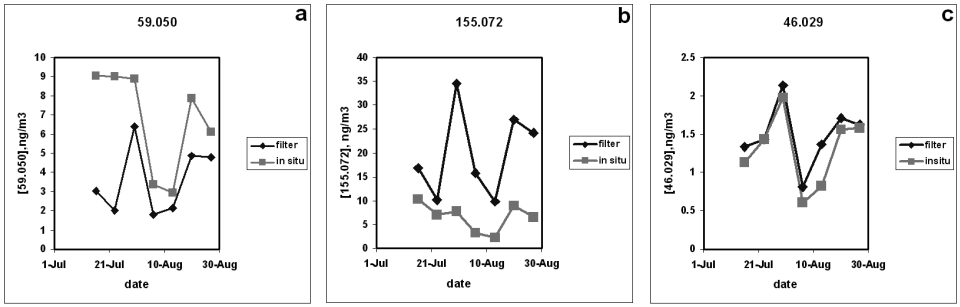

Figure 1: a) first case, in situ signal is higher than filter; b) second case, filter signal is higher than in situ; c) third case, filter signal is approximately equal to in situ one.

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Boeren-Leidse specialty cumin cheese compared to other cumin cheese using PTR-MS

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Abstract

The aim of the study was to compare characteristics of the Boeren-Leidse specialty cumin cheese with EU Protected Designation of Origin with those of other cumin cheeses of varying commercial Dutch brands. The characteristics selected were the headspace concentrations of the volatiles measured by high sensitivity proton-transfer mass spectrometry, because of their relationship with sensory (aroma) properties. The concentrations of the volatiles were used as fingerprints of the cheeses and patterns were subsequently explored by Principal Component Analysis (PCA). PCA showed clustering of the Boeren-Leidse cheese. Boeren-Leidse cumin cheese showed a distinct volatile profile. Many compounds were present at significantly higher concentrations in the headspace of the specialty cheese in comparison to the other cumin cheeses. The characteristic volatile compounds were tentatively identified by PTR-time-of-flight-MS.

Introduction

Artisanal and regional products are becoming increasingly popular. The integrity of these products is protected with an EU regulation that certifies a protected denomination of origin (PDO) [1]. In the Netherlands one of the first products that received a Protected Designation of Origin was traditional farmers' cheese from the surroundings of the city of Leiden ('Boeren-Leidse kaas met sleutels'). The Boeren-Leidse cheese is a semi-hard Dutch cumin cheese artisanally produced by farmers in the region of the city of Leiden and is appreciated for its rich cumin flavor and its firmness due to a low fat content of 30-40%.Traditional methods for verification of typicality and geographical origin do not always offer reproducible results and can be costly and time-consuming. Volatile profiling based on PTR-MS spectra is closely related to the traditional sensory characterization of cheese and can be used to identify markers of typicality and geographical origin in the profile of volatile organic compounds of the cheese and can serve as an efficient authentication tool [2]. The recent coupling of PTR-MS with time-of-flight spectrometers (PTR-TOF-MS) makes it possible to exploit the characteristics for the identification of the sum formula associated to the observed peaks [3], increasing the analytical information provided by PTR-MS. The aim of the present study was to investigate whether samples of PDO protected Boeren-Leidse cumin cheese could be discriminated from other Dutch cumin cheese samples by their volatile profiles as measured by High Sensitivity PTR-MS (HS PTR-MS). PTR-TOF-MS analysis was used for identification of the volatile compounds that characterize the specialty cheese.

Experimental

Two sets of cheese were obtained: one composed of samples of Boeren-Leidse cheese and one with samples of other Dutch cumin cheeses of varying brands. Cheese fat content and maturity were similar for both groups. The Boeren-Leidse cheese was manufactured under conditions specified in the production rules of the union of cheese farmers of Leiden [4]. Cubes of approximately 3 grams were equilibrated at 30 °C for 30 minutes. The volatile compounds were measured by HS PTR-MS, whereby a complete mass spectrum in the range of 20-150 atomic mass units (amu), at a mass detection rate of 0.2 s mass-1, was gathered in 26s. Analyses were carried out in independent triplicates and the data were background corrected. The averages of triplicate measurements were subjected to Principal Component Analysis (PCA; Pirouette 4.01, Infometrix, Seattle, WA). A one way analysis of variance was performed on the concentration data of the 60 most predominant ions in order to determine significant differences between the Boeren-Leidse cheese and the other cumin cheeses.

The volatile compounds of representative samples of both types of cheese, were tentatively identified using a PTR-TOF-MS 8000 instrument from Ionicon GmbH (Innsbruck, Austria) in its V mode configuration.

Results & Discussion

All samples were analyzed by PTR-MS. A mass spectrum of a characteristic Boeren-Leidse cheese sample is presented in Figure 1. Several ions were measured at considerable concentrations resulting in an interesting fingerprint of this specialty cheese.

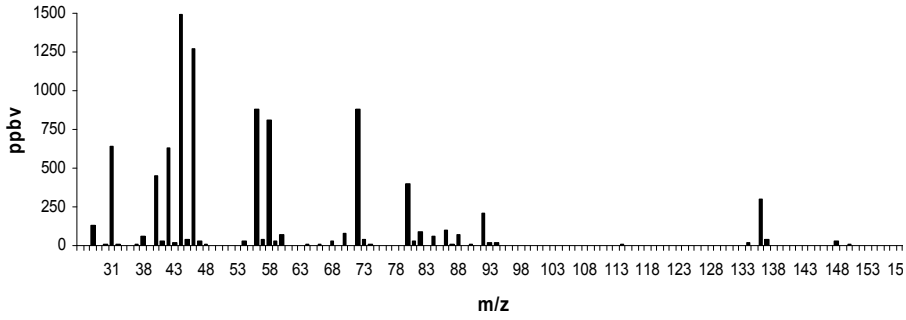

Figure 1: PTR-Mass spectrum of a characteristic Boeren-Leidse cheese sample.

Subsequently the averages of all cumin cheese samples were subjected to PCA in order to explore clustering of Boeren-Leidse and other cumin cheeses. A plot of the first three dimensions of PCA is presented in Figure 2. The PCA shows that Boeren-Leidse cheese samples cluster and are clearly discriminated from the other cumin cheese samples. These results are very promising from both characterization and authentication perspectives.

Characteristic samples were subsequently subjected to PTR-TOF-MS analysis in order to determine the identity of the volatile compounds characteristic for the Boeren-Leidse cheese tentatively. The four predominant compounds for the Boeren-Leidse cheese were ethanol (m/z 47.048), 2-butanone-butanal (m/z 73.063), p-cymene (m/z 137.129), and acetaldehyde (m/z 45.033). Compounds that discriminated the Boeren-Leidse cheese significantly (ANOVA, $P<0.05$) from the other cumin cheeses were especially some ketones, aldehydes, acids, and p-cymene.

Present results show that Boeren-Leidse cheese has a characteristic fingerprint of volatile compounds, which can be easily and rapidly measured by PTR-MS. Future studies will focus on the development of mathematical models which allow authentication of the Boeren-Leidse cheese based on their volatile fingerprints

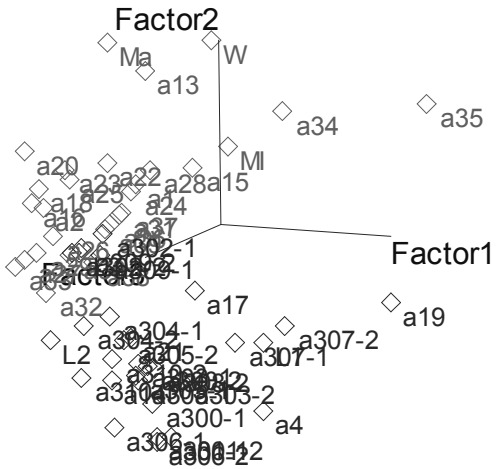

Figure 2: First three dimensions of the Principal Component Analysis on the mass spectral data of Boeren-Leidse cheese (blue) and other cumin cheeses (red).

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Measuring Partition Coefficients of VOCs and their Temperature Dependence by Dynamic Stripping and Proton-Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS)

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Abstract

Air-water partition coefficients play a significant role in understanding processes like aroma release from food, for many environmental phenomena or in medical analysis (breath analysis). The equilibrium of gas dissolved in a liquid (e.g. water) can be described via Henry's Law constant (HLC).

We have developed and validated a dynamic approach using a stripping cell configuration coupled on-line to a PTR-ToF-MS,[1-2] to measure with high accuracy the HLC of VOCs; see Fig.1. This methodology allows the rapid determination of water-air partition coefficients, even for molecules with low volatility, and over an extended temperature range (25-90 °C).

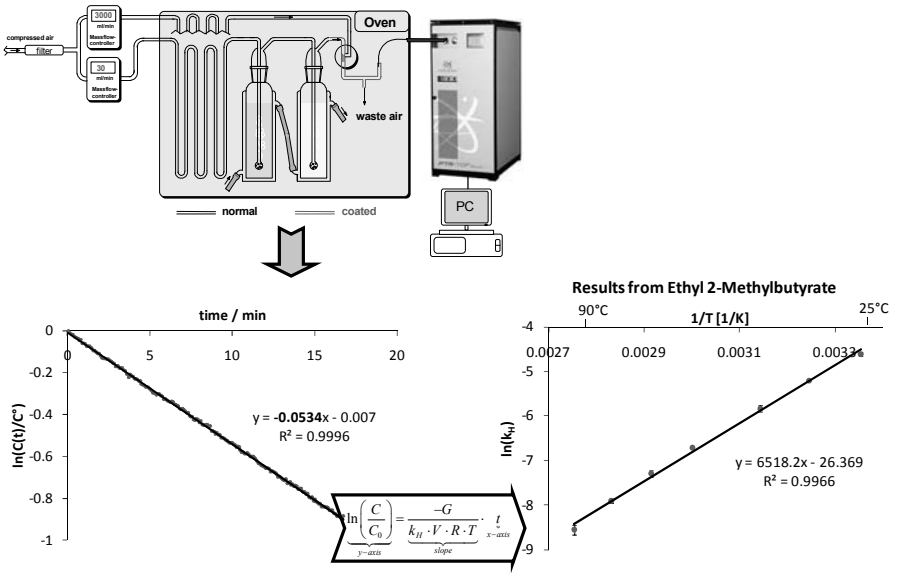

Fig. 1 Set-up for the measurement of partition coefficients using a PTR-ToF-MS; gasflow G, volume V, temperature T. Results are shown for Ethyl 2-Methylbutyrate

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PTR-MS measurement of VOCs during the 2010 Expo in Shanghai, China

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Abstract

PTR-MS was deployed at an urban site in Shanghai from April 20th to July 17th, 2010. Intercomparison between PTR-MS and GC-FID showed good agreements for most hydrocarbons. Emission ratios for VOCs species to CO were calculated by three methods: road tunnel measurements, a source-tracer-ratio method and multivariate regression. Very high emission ratios for OVOCs were determined in Shanghai, which is consistent with high percentages of OVOCs contributed from mobile vehicles (67.4%-73.4%).

Introduction

Shanghai is one of the most developed cities in China and has more than 19 million people and 2.7 million mobile vehicles. As the host city for the 2010 Expo, the air quality of Shanghai during the Expo was an issue of great concern.

Volatile organic compounds (VOCs) are precursors for the production of ozone and secondary organic aerosols (SOA). However, measurements of VOCs, especially those with a high time resolution, are very rare in Shanghai. Limited studies have shown that vehicle emissions, fuel evaporation and industrial solvent use are the sources of VOCs in Shanghai[1].

Experimental Methods

In this study, a proton transfer reaction mass spectrometer (PTR-MS) was deployed at an urban site in east of Shanghai (31.23N, 121.53E) from April 20th to July 17th, 2010. The PTR-MS was run at the standard mode with drift pressure at 2.20mbar and voltage at 600 V(equivalent to E/N=134 Td). Background signals were monitored by passing air through a Pt catalyst converter after every 300 cycles (about 2h) of ambient measurements. The PTR-MS measurements were calibrated using a gas standard every 2-3 days. The sensitivities for all VOCs species changed little throughout the entire campaign (RSD<10%).

Results

Intercomparison

Besides PTR-MS, an online GC-FID was deployed to measure NMHCs at the site. This provides a good opportunity to compare measurement results of aromatic compounds between the two

instruments. Figure 1 shows the correlations of PTR-MS results with GC-FID results. The correlations were strong for benzene, toluene and C8 aromatics and the slopes from linear fit were in the range of 0.89-1.34. There was a higher data scatter for the correlation of styrene (R=0.80) and the regression slope was 1.24.

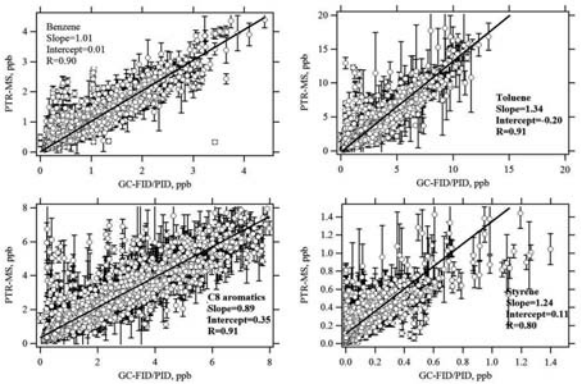

Figure 1: Correlations between aromatics measurements of PTR-MS and GC-FID.

Emission ratios relative to CO

Emission ratios of VOCs relative to CO were obtained from three method: road tunnel measurements, a source-tracer-ratio method and multivariate linear regression(only for OVOCs).

As a part of the campaign, 29 canisters were collected in 3 main tunnels near downtown area cross the Huangpu River. These canisters were shipped back to laboratory and analyzed VOCs and CO levels. The correlation coefficients between VOCs and CO were all higher than 0.8, except for MEK (0.74), acetone (0.61) and methanol (0.24). These compounds may be not conserved quantitatively in canisters. The emission ratios of VOCs were estimated from linear regressions. Since the correlations were low for acetone and methanol, their emission ratios were calculated as the average ratio of these two compounds.

The source-tracer-ratio (STR) method has been used to distinguish primary and secondary sources for OVOCs[3]. STR method first divides VOCs concentration into two parts: VOCs concentrations related to the tracer (CO) (VOC_{tracer}) and concentrations without relation with tracer (VOC_{other}). Then, a range of emission ratios of VOC to CO were tried and VOC_{other} were calculated from VOC, CO concentrations and emission ratio. Emission ratio was obtained when R^2 between VOC_{other} and CO reach its minimum. Bootstrap analysis were run for 100 times to estimate the uncertainties of determined emission ratios.

Multivariate linear regression was widely used in source appointment of OVOCs species, including formaldehyde and acetone. In this study, a linear model was established to determine emission ratios and contributions from different sources. The model is expressed as:

$$[OVOC]=K1*([CO]-[CO_{bg}]) +K2*[PAN]+K3*[Toluene_{ind}]+[bg] \quad (1)$$

Here, [OVOCs], [CO], [PAN] are the concentrations of OVOCs, CO and PAN. CO_{bg} is the background of CO concentration and it is estimated from the 5^{th} percentile of measured CO concentrations (0.29 ppm). $Toluene_{ind}$ is toluene concentration from industrial related solvent use. The $toluene_{ind}$ term is added here, because the two terms of CO and PAN cannot explain some

high peaks of measured OVOCs concentrations. Industrial sources were previously suggested to be important sources of VOCs[1]. $Toluene_{ind}$ was calculated from the enhanced concentrations above the tunnel fit line of toluene with CO. Other parameters, including K1, K2, K3 and [bg] are estimated from the fit.

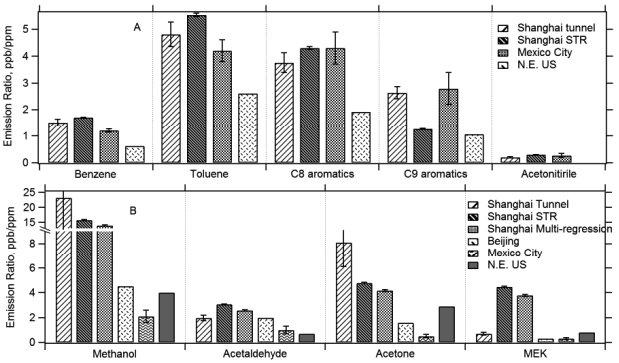

Figure 2: Emission ratios of NMHCs (a) and OVOCs (b) relative to CO calculated from Shanghai and comparison with other regions, including Beijing[3], Mexico City[4] and Northeast of US[5].

Figure 2 shows the estimated emission ratios for various VOCs in Shanghai. The emission ratios from the tunnel data and the STR method agreed well with each other for both NMHCs and OVOCs. The differences between the two method were lower than 50%, except for MEK. The emission ratios of MEK obtained from the tunnel data is 0.69±0.11, whereas the value from STR is 4.47±0.06. The reason for the discrepancy is unknown. The emission ratios from the multivariate regression method for OVOCs were close to those from the STR method.

It is interesting to compare our results with literature values for other cities. For NMHCs, emission ratios were similar to those estimated from Mexico City and were about twice of those from northeast US. This may reflects the difference in control measures and fleet age. However, The emission ratios for OVOCs in Shanghai were much higher than those from other regions, even higher than its companion city in China (Beijing). The abnormal high emission ratios for OVOCS will lead to unusual source attribution results, as shown below.

Source Attribution of OVOCs

The source attribution results of OVOCs from multivariate linear regressions were shown in Figure 3 and Table 1. The CO term in equation 1 may come from internal combustion engines and biomass burning sources. Since acetonitrile/CO ratios were not enhanced above the ratio from tunnel data (not shown), as reflected by the similar emission ratios from ambient results and tunnel measurements, we conclude that biomass burning was not a significant source of VOCs emissions during the entire campaign. Thus, the CO term is attributed to internal combustion engines. The other two terms are attributed to secondary formation and industrial emissions, respectively. Mobile emissions accounted for more than 65% for the all four OVOCs species. Secondary sources only contributed 16.3%-25.7% of the total emissions. Industrial emissions occurred in irregular peaks and their contributions were in the range of 6.1%-14.5%. The high

OVOCs emission ratios and source proportions from mobile vehicles could play an important role in ozone and SOA formation chemistry in Shanghai.

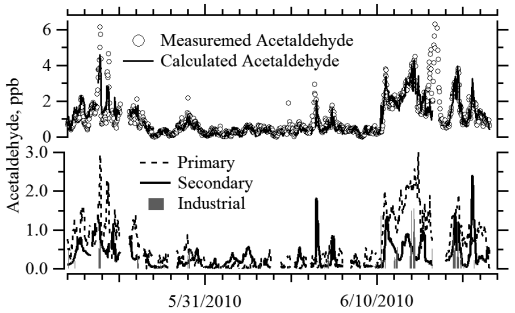

Figure 3: Measured and calculated concentrations of acetaldehyde in 17 May- 16 June, 2010.

Table 1: Correlation coefficients (R) for measured and calculated OVOC concentrations and the percentages of OVOCs from different sources

Compounds	*R*	*Mobile Vehicle(%)*	*Secondary(%)*	*Industrial(%)*
Methanol	0.79	73.4	16.3	10.3
Acetaldehyde	0.81	67.4	22.4	10.2
Acetone	0.82	68.2	25.7	6.1
MEK	0.76	67.4	18.1	14.5

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Air quality monitoring at a Western Australian rural location impacted by industrial and transport infrastructure emissions

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Abstract

Trace atmospheric VOC were monitored in Yarloop, a rural location about 150 Km South of Perth (WA) for 76 days during spring and summer '08 -'09 and for 128 days of winter and spring '09. Besides the biogenic and biomass burning sources characteristic of the rural Australian environment, the site is impacted with emissions from a nearby isolated alumina refinery, a heavy haulage and passenger railway line and a regional motorway.

Continuous ambient air monitoring was conducted by HS-PTR-MS operated in scan mode, (m/z 21-200 amu). Quality control was assisted by daily instrumental background check and fortnightly calibrations, both made with an ancillary Gas Calibration Unit (GCU-s) [1]. On a number of occasions, the PTR-MS measurements were associated with sampling and analysis of VOCs according to US EPA methods for carbonyls (method TO-11A), non-polar VOC (method TO-14 and TO-15), aromatic VOC and hydrocarbons (method TO-17) [2]. Results from the US EPA methods aided with the chemical identification of several ions detected by PTR-MS. During the winter '09 PTR-MS campaign the volume mixing ratios of NMHC, O_3, NO_x, CO, SO_2 and concentrations of $PM_{2.5}$ were also continuously monitored, along with a suite of meteorological parameters. Aerosol vertical measurements up to 2000m were conducted using ground-based ceilometer backscatter radar.

The mean diurnal cycles and seasonal differences in VOC levels at the site have been revealed and an interpretation attempted in light of meteorology, phenology and tropospheric chemistry. The winter '09 database of atmospheric mixing ratios for selected PTR-MS masses of interest has been further analysed in conjunction with the highly time-resolved air quality and meteorological parameters. The pattern of underlying relationships in this multivariate dataset was explored with statistical methods. Performing principal component analysis – PCA [3] aided with the identification of diverse atmospheric sources and processes impacting the air at the site. The regression analyses on the VOC and other pollutant concentrations during short-term events, when compared with known emission ratios from pollution inventories and literature, resolved the contribution from industrial, traffic-related or biomass burning sources impacting the site.

The results obtained from the Yarloop 2008-2009 campaign builds on and expand the knowledge gained from previous CSIRO [4] and DEC [5] studies in the area, shedding light on the interplay between local meteorology, biogenic and anthropogenic VOC sources and perceived air quality issues in this representative rural Western Australian location.

Figure 1: the site of air quality study with PTR-MS and ancillaries in south-western Australia is a receptor of emission from native vegetation, biomass burning, farming activities, an isolated alumina refinery, motorway and railway traffic.

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