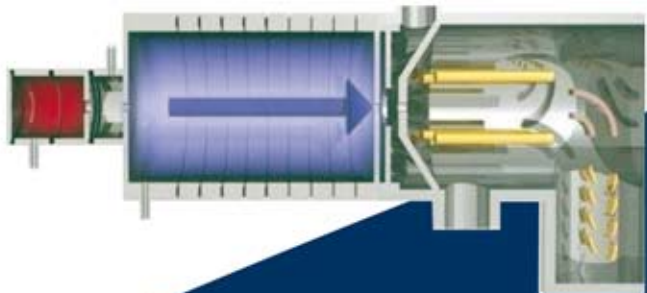Armin Hansel, Jürgen Dunkl
Contributions

6th International Conference on
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Mass Spectrometry and its Applications
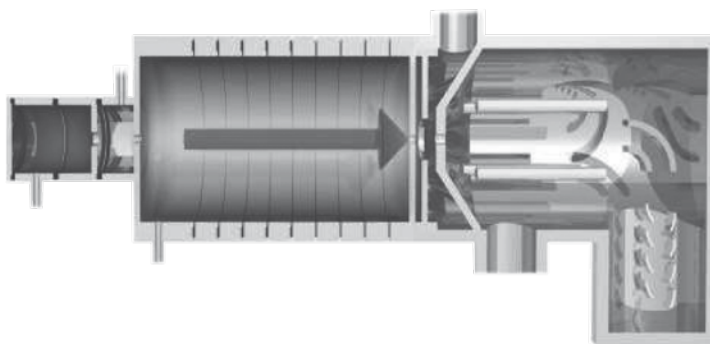
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Armin Hansel
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6th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications

Contributions

Editors:
Armin Hansel
Jürgen Dunkl

Institut für Ionenphysik und Angewandte Physik
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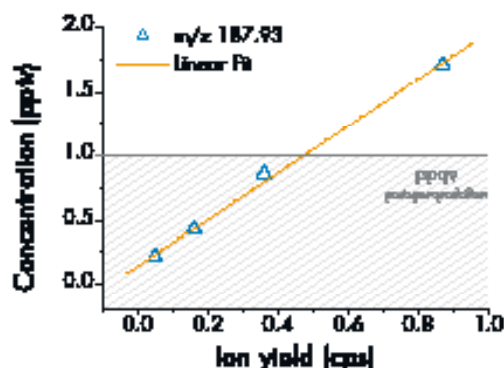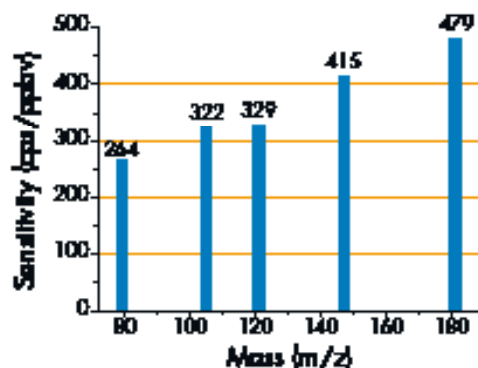
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Contents

Applications in Medicine and Biotechnology

Applications in Food Science

Instruments & Technology and Future Trends

Applications in Environmental Science

Contributed Papers (Posters)

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 late 1990's. PTR-MS has been found to be an extremely powerful and promising technology for the in-situ detection of volatile organic compounds (VOCs) at trace levels (pptv) in gaseous media. PTR-MS has been successfully employed in many fields of research & technology including environmental research, life sciences, and food science.

Almost 15 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 many research institutions and companies use this technology throughout the world.

The intent in initiating and organizing the 1st International PTR-MS Conference in January 2003 in Igls, Austria was to bring together active scientists and technology experts involved in mass spectrometric measurements of VOCs. The 6th 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 100 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 keynote speakers presenting interdisciplinary overviews in environmental science, food science and medicine. On the following days the conference topics PTR-MS in Environmental Science, Food Science, Medicine & Biotechnology, will be discussed in parallel sessions.

In the framework of the 6th PTR-MS Conference we organize for the very first time a IONICON PTR-MS and PTR-TOF-MS User Day dealing exclusively with your experiences, questions and problems concerning the PTR-MS technology. The topics and the content of this User Day will be determined solely by the attending PTR-MS users. An external expert panel, IONICON experts, as well as the whole audience will discuss your hot topics and burning questions, but also highly specific cases in several thematically grouped sessions.

I would like to thank the session chairs Isabelle Déléris and Jean-Luc Le Quéré (Food Science), Jens Herbig and Wolfram Miekisch (Medicine and Biotechnology) and Philipp Sulzer (PTR-MS User Day) 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, who worked very hard to organise this conference. Finally I would like to thank the UNIVERSITY of INNSBRUCK, IONICON ANALYTIK, IONIMED ANALYTIK 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 2013

Applications in Medicine
and Biotechnology

The State of Breath Analysis: Achievements and Challenges, Consequences for Applications

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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).

Around 1000 compounds appear in exhaled breath. For many of them it is unclear if they are endogenous or exogenous (or both). Some of them are produced by bacteria in the gut (e.g. hydrogen or methane). Additional information is available through investigation of the headspace of urine. Compounds appearing in exhaled breath *and* in urine are suspected to be systemic, i.e., to be contained in blood and being excreted through both, breath and urine. Supplementary biochemical information can be achieved by investigation of the headspace of cell and bacterial cultures. For some very few specific compounds, more detailed information has been gained through *real-time* analysis of exhaled breath while exerting effort on an ergometer or during sleep: examples of such compounds are acetone, isoprene, dimethylsulfide, methyl acetate or 2-pentanone [1].
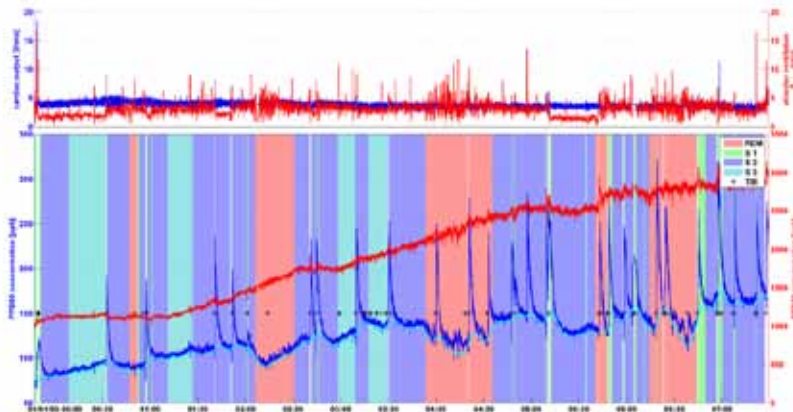
Figure 1: An example of a real-time measurement of acetone and isoprene during sleep is presented in the following Figure (see also Ref [2]), referring to one night of a healthy volunteer.

The concentrations of acetone (red, right y-axis) and isoprene (blue, left y-axis) are presented in the lower panel of the figure, together with the sleep stages (light sleep stage 1, deep sleep stages 2 and 3 and **R**apid **E**ye **M**ovement sleep REM). Acetone and isoprene behave very differently [2]. The concentration of acetone does usually increase in a relatively smooth manner overnight. The concentration of isoprene increases, too, but less pronounced than acetone. In addition, isoprene shows a very characteristic peak structure. These peaks are related to movements of the body or changes in sleep stage. Isoprene is not only produced in the liver, but also in the periphery of the human body (e.g., in the legs or in the arms). The periphery of the body can selectively be depleted from isoprene, by exerting effort with only the left (right) leg or only the left (right) arm [3-4]. Each exertion of effort leads to a pronounced peak in isoprene. An increase of isoprene concentration in exhaled breath is even produced by a few leg (or arm) contractions, without exerting real effort.

Cell culture investigations reveal that different cell types can release or consume different volatile compounds. Examples of cell types investigated are the lung cancer cell lines NCI-H2087, NCI-H1666, A549 and CALU-1, or the non-cancerogenous cell lines HBEpC and hFB [5]. Compounds released are hydrocarbons (e.g. 2,3,4-trimethylpentane, octane or 4-methylheptane), alcohols (e.g., 3-methyl-1-butanol, ethanol or 2-methyl-1-propanol), esters, acetone and 2-pentanone. Aldehydes and n-butylacetate, on the other hand, are often consumed by cells. Non-cancerogenous cells display a tendency to release a broader spectrum of compounds than cancer cells.

Bacteria often produce considerable amounts of volatile compounds. A particular focus of interest are bacteria which lead to lung inflammation, such as *Streptococcus pneumonia, Haemophilus influenza, Pseudomonas aeruginosa or Staphylococcus aeruginosa* [6-8]. Many of these compounds are not usually observed in exhaled breath and could therefore be used for diagnosis of lung inflammation [8]. Since breath can be sampled as often as it is desirable, and since *real-time* measurement of exhaled breath is feasible, this might lead to a *real-time* detection of lung inflammation.

The investigation of exhaled breath of cancer patients is a particular focus of research [9-10]. Even though interesting pilot results have been achieved, this still needs detailed studies with more information on the volatile compounds observed. Some compounds appear in higher concentrations in cancer patients as compared to healthy volunteers, whereas other compounds (like isoprene) show lower concentration in exhaled breath of cancer patients. The specific example of isoprene may be related to medication or be due to a genuine decrease of isoprene production rate in the human body.

Portable hand-held devices allowing real-time measurement of exhaled breath would be particularly interesting for medical applications in clinical routine. Even though some devices exist (such as a hand-held device for nitric oxide measurement in exhaled breath for asthma monitoring), the use of volatile compounds in clinical routine is still in its infancy. One of the most promising approaches for clinical routine is the ingestion of isotopically labeled precursor compounds (such as 13C-labeled uracil [11]) which are metabolized to 13CO2, whose concentration can be determined in exhaled breath [12]. The respective infrared

spectrophotometers are comparatively small portable instruments giving very reliable measurement results.

The use of volatiles in different fields of research is still at its very beginning. The appearance of volatiles in breath, urine, feces or sweat has considerable diagnostic potential. It is by combination of the results achieved through GCMS and *real-time* direct mass spectrometric methods such as PTR-TOF that fast identification and quantification can be achieved. Also

information on volatiles released (or consumed) by cell and bacterial cultures will help to bring breath tests into routine clinical applications. The use of isotopically labeled compounds for measurement of enzyme activity with breath tests based on exhaled 13CO2 and other volatile target compounds is particularly impressive. This offers the possibility of non-invasive phenotyping, thereby complementing genetic tests and opening up the way to a "personalized" medicine.

References

[1] King et al., Dynamic profiles of volatile organic compounds in exhaled breath as determined by a coupled PTR-MS/GC-MS study. Physiol Meas 31, 1169 – 1184 (2010)

[2] King et al., Measurement of endogenous acetone and isoprene in exhaled breath during sleep, Physiol Meas 33: 413-428 (2012)

[3] King et al., Breath isoprene: muscle dystrophy patients support the concept of a pool of isoprene in the periphery of the human body. Biochemical and Biophysical Research Communications 423 (3): 526-530 (2012)

[4] Mochalski et al., Human blood and plasma partition coefficients for C4-C8 n-alkanes, isoalkanes and 1-alkenes. Int J Toxicology 31: 267-275 (2012)

[5] Filipiak et al., TD-GC-MS analysis of volatile metabolites of human lung cancer and normal cells in vitro. Cancer Epidemiology Biomarkers and Prevention 19(1): 182-95 (2010)

[6] Filipiak et al., Molecular analysis of volatile metabolites released specifically by Staphylococcus aureus and Pseudomonas aeruginosa. BMC Microbiology 12 (1): 113 (2012).

[7] Filipiak W et al., Characterization of the release and uptake of volatile metabolites from Streptococcus pneumoniae and Haemophilus influenzae by gas chromatography mass spectrometry. To appear in: Microbiology (2012)

[8] Filipiak W et al., Volatile organic compounds (VOCs) released by pathogenic microorganisms in vitro: Potential breath biomarkers for early-stage diagnosis of disease. To appear in: Amann A and Smith D, eds. Volatile biomarkers: non-invasive diagnosis in physiology and medicine. Elsevier, Amsterdam (2013)

[9] Bajtarevic et al., Noninvasive detection of lung cancer by analysis of exhaled breath. BMC Cancer 9: 348 (2009)

[10] Hakim et al., Formation of Volatile Organic Compounds Associated with Lung Cancer and Suspected Metabolic Pathways. To appear in: Chem Rev (2012)

[11] Mattison et al., Rapid identification of dihydropyrimidine dehydrogenase deficiency by using a novel 2-13C-uracil breath test. Clin Cancer Res (2004)

[12] Modak, Barriers to overcome for transition of breath tests from research to routine clinical practice, J Breath Res 5: 030202 (2011)

Volatile Organic Compounds in the Exhaled Breath of Asian Volunteers

Shruti Pavagadhi and <u>Rajasekhar Balasubramanian</u>

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In recent years, the determination of concentration profiles of volatile organic compounds (VOCs) in human exhaled breath has gained considerable biomedical and clinical importance as some of these compounds have been linked to lung disease, inflammatory and malignant processes in the body. Endogenous VOCs are released within the human organisms as a result of normal metabolic activity and/or due to pathological disorders. These VOCs enter the blood stream, and are eventually metabolized, or excreted via exhalation, skin emission, urine, etc. An exhalation gas sample of an average person contains hundreds of VOCs with volume concentrations ranging from parts per trillion (pptv) to parts per million (ppmv). Identifying the emission patterns of VOCs in human breath could therefore offer valuable information for routine clinical applications for diagnosing a range of pathological conditions and diseases among patients in need of medical help. A number of recent studies reported that PTR-MS (Proton Transfer Reaction-Mass Spectrometry) has potential to be used as an analytical tool for a rapid determination of VOCs in human breath. However, the previous studies conducted with PTR-MS have been restricted to Europe and North America. In the present study, the potential use of PTR-MS as a non-invasive technique for determination of VOCs in human breath was explored among healthy Asian volunteers for the first time. Volunteers from different ethnic and age groups of Asians participated in the study. A total of 42 VOCs were monitored at a single time point among all the healthy volunteers. VOCs with high abundance were subsequently monitored in a multi-time point mode among selected volunteers by taking into consideration their day-to-day activity patterns and also the intensity of some of their specific activities such as exercise and occupational exposure. The implications of results obtained from this preliminary study will be discussed.

Non-invasive detection of renal function via breath gas analysis: A potential biomarker for organ acceptance?

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Abstract

Breath gas analysis is an emerging field that attempts to link components in exhaled breath gas with state-of-health or illness [1]. This is based on the premise that disease in the body will elicit abnormal biochemical reactions which in turn produce chemical compounds that might be excreted by the body – at least in part – via exhalation. We used PTR-MS to directly sample and analyse selected VOC constituents in the exhaled breath of patients (n=96) undergoing kidney transplantation. Breath samples were taken before surgery and then over an extended period thereafter. Comparison of PTR-MS data with routine blood-serum data revealed a specific compound (ion trace) at *m/z* 115 that correlated with creatinine in blood serum and daily urine production, which are the current generally-accepted markers for kidney function. PTR-TOF analyses revealed that this compound had an exact molecular mass of 114.104 u and a chemical composition of $C_7H_{14}O$. Subsequent analyses using PTR-QqQ-MS suggested the compound to be a C_7-ketone or branched C_7-aldehyde. It is hoped that the results of this study will provide impetus to other researchers in the field to further delve into the nature of this compound and its possible biochemical production routes to ascertain the eligibility of this compound for potential use in future routine breath analysis for renal function assessment.

Introduction

The kidneys' function is to filter the blood from many hundreds of compounds, which are then metabolised and/or excreted via the urine. Loss of kidney function is a life-threating situation that must be treated with dialysis and ultimately with renal transplantation. Although many thousand such procedures are regularly carried out throughout the world, currently there is no established biochemical marker that allows rejection of the transplanted organ to be identified at the very early stages of such episodes. Furthermore, current parameters used for assessing kidney function

involve invasive sampling of blood. Discovery of such a marker would therefore allow appropriate treatment to be given much earlier, thereby increasing the likelihood of foreign organ acceptance by the body.

Over the years, PTR-MS has become an established tool in the field of breath gas analysis due to its direct, real-time sampling capabilities [2]. This on-line aspect of measurements not only allows for a fast throughput of samples, but also avoids the complications and often error-prone off-line analyses when measuring gas samples collected in Tedlar/Teflon bags [3]. The present study aimed to establish whether the exhaled breath gas of renal graft patients might offer a non-invasive biomarker for organ rejection episodes.

Study design

All patients gave written informed consent before participation in this study. In total, 96 patients (mean age 48±14 years; 30 % female) provided 642 breath samples over the course of the study. A high sensitivity PTR-MS (hs-PTR-QMS) was used for direct sampling of breath. A Teflon PFA tube of 1" outer diameter was connected transversely to the PTR-MS inlet capillary using a suitable fitting. Patients were required to inhale and exhale continuously through this ~10 cm long tube, during which time PTR-MS sampled from the centre of the tube; this configuration was the basis for the later development of the buffered end-tidal sampler (BET) [4]. The PTR-MS was connected to a 230 V uninterruptible power supply (UPS), allowing the instrument to be wheeled to the patients' bedsides (located in different rooms of the hospital). Measurements were made in MID mode with a selection of 41 m/z per test. This selection was made to reduce the time per patient to a tolerable and manageable period, and compounds were chosen based on results of a preliminary screening. The study lasted for 12 months. At the end of the *in-situ* measurements, additional breath gas samples from selected patients were collected in 1 L Silcosteel™ canisters (Restek, Bellefonte, PA) using a breath collection unit (BCU) (Ionimed Analytik, Innsbruck, Austria) and were analysed in the laboratory using PTR-TOF and PTR-QqQ-MS to further ascertain the nature of the identified marker compound.

Results

PTR-MS results indicated one particular compound – detected at *m/z* 115 – that correlated with the established kidney function markers creatinine and daily urine output. Correlation of this identified breath maker with creatinine is exemplarily shown in figure 1 for all patients approximately one week after surgery. Typically, low creatinine levels in the blood resulted in low concentrations of *m/z* 115 in exhaled breath. When creatinine levels increased, so too did *m/z* 115, with the latter often increasing earlier than the established blood marker, indicating a deterioration in kidney function.
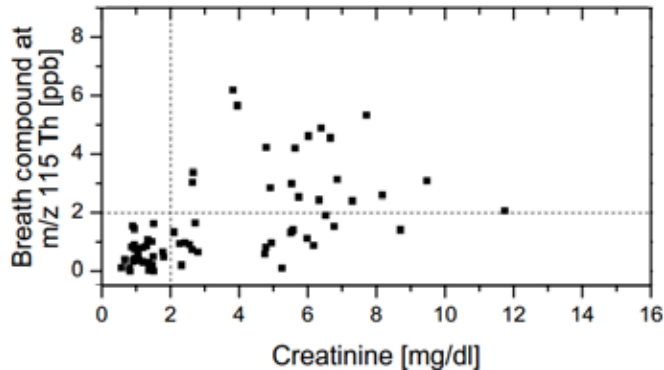
Figure 1: Correlation plot of the identified breath marker at m/z 115 and blood-serum creatinine. Data are from all patients approximately one week after surgery.

Figure 2 shows data for one individual over the course of recovery from surgery. Organ transplantation took place on day 0. Here it can be clearly seen that as the kidney function improves, as indicated by the amount of urine produced, creatinine and the breath marker at *m/z* 115 decrease.
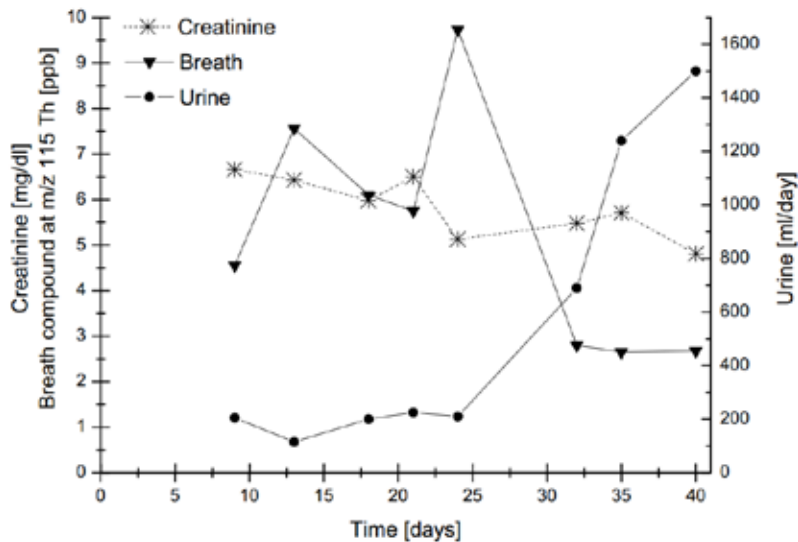
Figure 2: Exemplary data of blood-serum creatinine concentration, daily urine output, and concentration of the exhaled breath marker at m/z 115 for one patient. Here, the breath marker follows a similar pattern to creatinine, both of which decrease as kidney function increases, as indicated by the rise in urine production.

Outlook

The finding of the ion trace at m/z 115 that significantly correlates with the established renal function biomarkers provides a building block for further establishing the nature of this compound. First and foremost, the origin of this compound must be carefully elucidated to rule out possible exogenous sources, since a recent study has suggested that a compound of this nature might be derived from haemodialysis [5]. Once this has been established and the identity of the compound has been determined unequivocally, focussed studies can investigate the sensitivity of this compound to changes in kidney function, with the ultimate aim of generating enough evidence to include non-invasive breath analysis to monitor renal function after organ transplantation, thus offering a parameter for early detection of a deterioration in functionality of the newly-transplanted organ that might ultimately lead to rejection of the organ. The hope is that monitoring such a biomarker might offer physicians the opportunity to implement adequate countermeasures as early as possible to improve organ acceptance by the body.

Acknowledgements

References

[1] A. Amann and D. Smith (eds.), Breath Analysis for Clinical Diagnosis and Therapeutic Monitoring, World Scientific Publishing, Singapore, (2005).

[2] J. Herbig and A. Amann, Proton Transfer Reaction-Mass Spectrometry Applications in Medical Research, Journal of Breath Research 3, 020201, (2009).

[3] J. Beauchamp, J. Herbig, R. Gutmann and A. Hansel, On the use of Tedlar bags for breath-gas sampling and analysis, Journal of Breath Research 2, 046001, (2008).

[4] J. Herbig, T. Titzmann, J. Beauchamp, I. Kohl and A. Hansel, Buffered end-tidal (BET) sampling - a novel method for real-time breath-gas analysis, Journal of Breath Research 2, 037008, (2008).

[5] N. Pagonas, W. Vautz, L. Seifert, R. Slodzinski, J. Jankowski, W. Zidek and T. H. Westhoff, Volatile Organic Compounds in Uremia, PLoS ONE 7, e46258, (2012).

PTR-MS applications in olfactology: detection of odorants at the human nasal receptor sites

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Abstract

PTR-MS was used to assess the delivery of the compound 1-butanol to the human olfactory receptor sites according to a standardised protocol using pens containing this odorant. Initial direct measurements of the pens themselves were made to validate the linearity of the concentration ranges employed. Subsequently, the PTR-MS inlet was positioned intranasally at the olfactory cleft of human subjects (n=35) to detect 1-butanol at varying concentrations during natural sniffing. The detected signal was compared to the presented concentration and the subjects' ability to perceive it. Furthermore, the mode of sniffing was varied for the pen with the highest concentration to assess its influence on the intranasal concentration and perception.

Introduction

Over the years PTR-MS has seen deployment in countless diverse situations from helicopter flights, balloon hoists, mountain hikes, jungle explorations, to arctic expeditions, and has sampled gases from processing plants, fermentation tanks, chemical warfare agents, illicit drugs, vehicle exhaust, food headspace, and the breath of mouse, dog, pig and human, to name but a few. A less explored territory for PTR-MS is the human nose. This cavernous odorant-exposed region of the olfactory organ offers a wealth of information relevant to both sensory science and olfactology. For the former, investigations can extend our knowledge on flavour perception during food consumption, e.g. by following flavour release profiles during mastication (e.g. [1]). For the latter, assessments can shed light on olfactory function – or dysfunction. With this in mind, PTR-MS was used to trace odorants directly within the nose over a range of concentrations presented at the nostril in a manner similar to clinical assessments for inter-comparison of intranasal concentrations, as well as comparison with sniffing behaviour and odorant perception of subjects.

Validating odorant delivery tools

Ear, nose and throat (ENT) specialists have several tools for assessing olfactory function and diagnosing anosmia, i.e. the loss of smell, which range in function, complexity and cost. A simple – yet very effective – test method for general anosmia is the so-called Sniff Magnitude Test

(SMT) [2]. This test is based on the premise that a person will automatically reduce their sniff intensity when presented with a malodour compared to an odourless sample. By measuring nasal inspiratory pressure, a loss of smell is established if no difference between the two conditions is observed. The University of Pennsylvania Smell Identification Test (UPSIT) offers a different approach by employing a forced (multiple) choice identification of a variety of odours using 'scratch and sniff' samples [3]. The forced choice aspect allows resulting answers to be screened for chance (i.e. guessing), thereby providing an indication of the subject's ability to both detect and correctly identify the odours. One of the most sophisticated tools available to the ENT physician is the olfactometer, which is an instrument designed to generate and deliver odorant pulses of specific duration and intensity and can be used simultaneously with functional magnetic resonance imaging (fMRI) or electroencephalography (EEG) for monitoring brain response to the odorant stimulus [4]. However, validation assessments using PTR-MS recently demonstrated that delivery of odorants by this system varies according to pulse duration and physicochemical properties of the odorant, and may exhibit large temporal variations that must be accounted for when using this system for diagnostic purposes [5]. Odorant pens – commercially available and known as Sniffin' Sticks – offer a cheap yet effective alternative to the olfactometer for olfactory function testing and are available for either individual or combined assessments of odour identification or discrimination, and olfactory sensitivity [6]. This study focussed on the latter set.

Sniffin' Sticks

A Sniffin' Stick odour threshold test set consisting of 17 pens containing 1-butanol in a 1:2 v/v dilution series at concentrations ranging from 8 % to 1.2 ppm_v (v/v) was used. Before carrying out tests with human subjects the pens were assessed for odorant concentration linearity by direct measurement with PTR-MS. These validation tests confirmed that 1-butanol concentrations followed an expected linear behaviour over the entire range of pens, as depicted in figure 1.
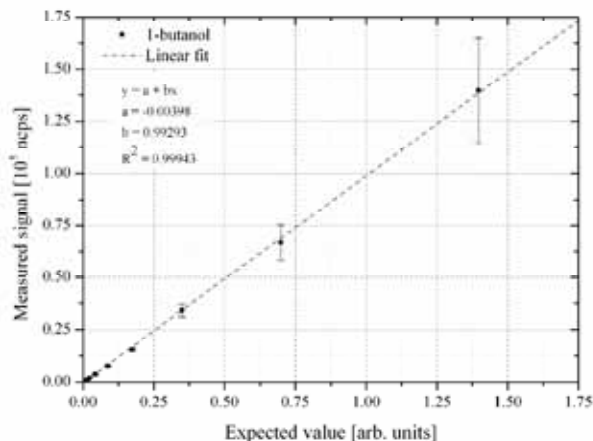
Figure 1: Linearity validation of Sniffin' Stick odour threshold set containing 1-butanol at varying concentrations from 1.2 ppm_v to 8 % (v/v). Each data point represents triplicate measurements of a single pen (i.e. at one specific 1-butanol concentration). The expected values were calculated relative to the PTR-MS signal of the pen with the highest concentration.

Tracing odorants within the nasal cavity

Human test subjects (n=35; 21 female, mean age 32±7 years) were fitted with a ~15 cm long PVC catheter that was placed under endoscopic direction at the olfactory cleft in the nose. The other end of this cannula was connected via a short length of 1/8" OD PFA tubing to the 1/16" OD Silcosteel inlet of the PTR-MS for detection of odorant concentrations near the epithelial cells. The PTR-MS inlet flow was set to 500 sccm and the inlet temperature was 80 °C. A cannula fitted at the subject's nostrils and connected to a pressure transducer allowed inspiratory nasal pressure and thereby the breathing cycle to be monitored throughout odorant presentation episodes.

Initial measurements of pure 1-butanol revealed the most abundant product analyte to be *m/z* 57. This signal was measured with a dwell time of 50 ms alongside *m/z* 21 (50 ms), *m/z* 37 (20 ms) and *m/z* 59 (50 ms). The latter signal relates to endogenous acetone and was used to monitor the breathing cycle of the subject in addition to the nasal pressure variations delivered by the pressure transducer. The analogue output signal of the latter was connected to an analogue input channel of the PTR-MS and was monitored within an MID cycle. An additional analogue input channel allowed a trigger signal to manually indicate the exact period of odorant pen presentation (operated by the presenter). The measurement frequency of these measurements of four *m/z* and two AIs amounted to just under 3.4 Hz.

Intranasal concentrations and olfactory perception

At the beginning of the odour presentation protocol the pen with the highest concentration (8 % v/v 1-butanol) was presented to ensure the subject was able to smell the odour they would be asked to detect, followed by presentation of six pen triads (v/v concentrations of 0.125, 0.25, 0.5, 1, 2, 4 and 8 %). Each triad consisted of an odorant target pen and two 'odourless' blanks (in random order). Subjects were required to identify the odorant-containing target pen of each triad. Target pens increased from lowest to highest concentration up to the maximum (figure 2).
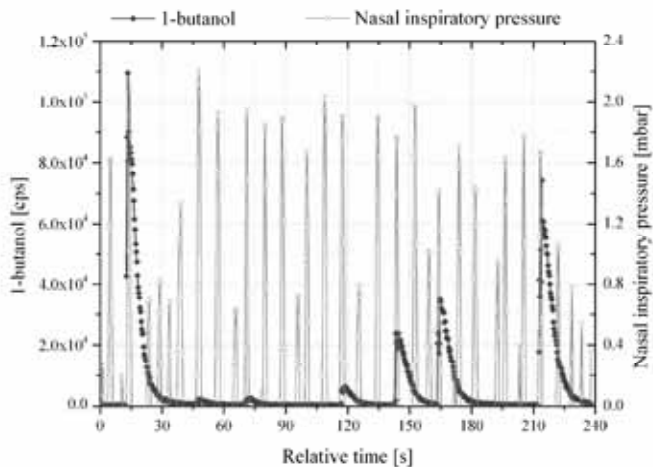
Figure 2: Intranasal concentration of 1-butanol (m/z 57) for one subject over a range of six odorant pen concentrations. Note that the first and last peaks are from the same pen (8 % v/v). Nasal inspiratory pressure is depicted on the right-hand y-axis.

Figure 2 exemplarily shows the intranasal 1-butanol signal of one test subject during a presentation protocol. As can be seen in this example, intranasal concentrations mirrored the increasing concentration of the target pens. This particular subject was unable to distinguish the two lowest target concentrations (here at t ~45 and ~70 s, respectively) from the blank pens. All subsequent target concentrations (from t ~120 s) were identified correctly.

Summary

These studies are a first attempt to correlate odour perception with the absolute concentration of an odorant that reaches the olfactory receptor sites and are a stepping-stone for further studies along this path, which will provide insights into olfactory function (or dysfunction) as well as aroma perception during food consumption. A future focus should be to try to investigate and clarify to what extent odorant molecules of different physicochemical properties are 'lost' during their passage through the nasal cavity and to ascertain the amount that reach the epithelial cells. With so many factors involved in these processes (e.g. [7]), such studies should shed some light on the processes involved.

Acknowledgements

References

[1] M. Mestres, N. Moran, A. Jordan and A. Buettner, Aroma release and retronasal perception during and after consumption of flavored whey protein gels with different textures. 1. *in vivo* release analysis, Journal of Agricultural and Food Chemistry 53, 403-409, (2005).

[2] R. A. Frank, M. F. Dulay and R. C. Gesteland, Assessment of the Sniff Magnitude Test as a clinical test of olfactory function, Physiology & Behavior 78, 195-204, (2003).

[3] R. L. Doty, P. Shaman and M. Dann, Development of the university of pennsylvania smell identification test: A standardized microencapsulated test of olfactory function, Physiology & Behavior 32, 489-502, (1984).

[4] G. Kobal, Pain-related electrical potentials of the human nasal mucosa elicited by chemical stimulation, Pain 22, 151-163, (1985).

[5] J. Beauchamp, J. Frasnelli, A. Buettner, M. Scheibe, A. Hansel and T. Hummel, Characterization of an olfactometer by proton-transfer-reaction mass spectrometry, Measurement Science and Technology 025801 (2010).

[6] T. Hummel, B. Sekinger, S. R. Wolf, E. Pauli and G. Kobal, 'Sniffin' Sticks': Olfactory Performance Assessed by the Combined Testing of Odour Identification, Odor Discrimination and Olfactory Threshold, Chemical Senses 22, 39-52, (1997).

[7] A. Buettner and J. Beauchamp, Chemical input - Sensory output: Diverse modes of physiology-flavour interaction, Food Quality and Preference 21, 915-924, (2010).

Realtime measurement of volatile components in the bioreactor via proton transfer reaction mass spectrometry (PTR-MS) – an approach for advanced bioprocess monitoring

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Abstract

Proton Transfer Reaction Mass Spectrometry (PTR-MS) technology was implemented for online monitoring of volatile organic compounds (VOCs) in the offgas of bioreactors. Focus was on the development of an interface between the bioreactor and the PTR-MS suitable for continuous sampling of VOCs produced by the bioprocess.

Introduction

The major bottleneck on the way to rational bioprocess design and control is the complexity of bioprocesses with living cells as production systems. Realtime access to physiology relevant process variables is very limited since biological systems additionally constrain direct measurements. Analytes which are accessible via analysis of the fermenter exhaust gas are volatile organic compounds. These VOCs arise as a result of microbiological activity during a fermentation process. PTR-MS technology perfectly matches the required high sensitivity for VOC measurements and a linearity range of multiple orders of magnitude.

Experimental Methods

Recombinant protein production processes with E. coli as model system [1] were used to asses the potential of PTR-MS based VOC measurements in bioprocess monitoring. For this purpose an interface between the bioreactor and the PTR-MS suitable for continuous sampling of VOCs emanating from the bioprocess has been developed.
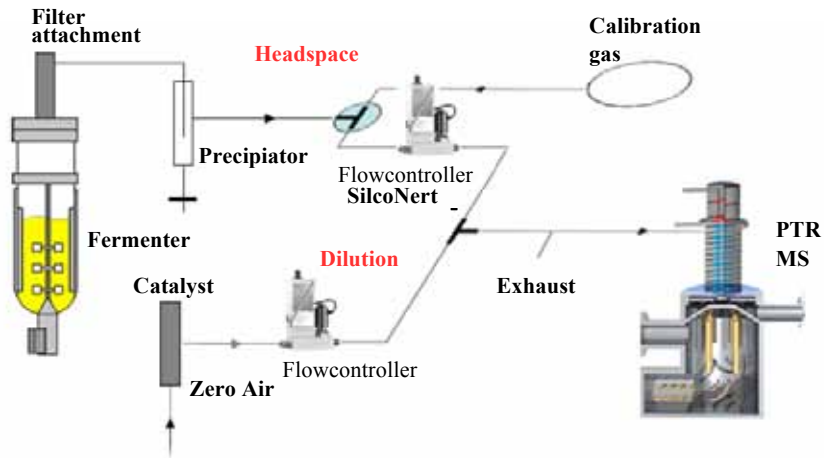
Figure 1: Simplified schematic of the setup. Fermenter off-gas is sampled and analyzed continuously. The inlet box is thermally controlled and allows for dilution and calibration and, if needed, multiplexing to analyze several fermenters.

Results

Reproducibility

To demonstrate the proper functionality of the inlet system, three identical E. coli fermentations were conducted. The reproducibility of these experiments can be shown by comparison of a set of typical PTR-MS signals (Figure 2).
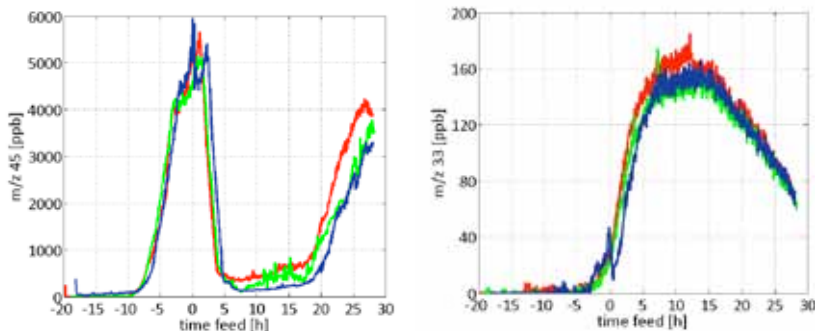
Figure 2: Typical PTR-MS signals from three recombinant E. coli fed-batch cultivations. Copyright 2012 Wiley. Used with permission from [1]

VOC based Process Information

Recombinant gene expression yields in a metabolic overload. Hence, growth rates decline (cell dry matter CDM deviates from the calculated course) and the consumption of glucose is reduced. This coincides with the increase of acetaldehyde and ethanol, which can be directly

visualized in the PTR-MS signals. Acetaldehyde and ethanol are known to be produced within mixed acid fermentation of *E. coli as* result of glucose accumulation (Figure 3).
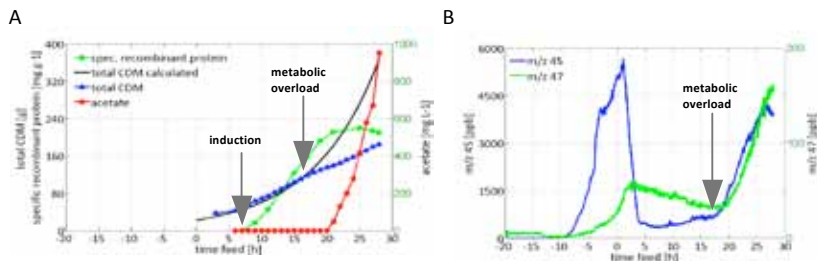
Figure 3: Recombinant E. coli fed-batch cultivation: (A) courses of calculated and total CDM, specific recombinant protein, and acetate; (B) courses of m/z 45 and 47 representing acetaldehyde and ethanol. Copyright 2012 Wiley. Used with permission from [1]

Discussion

It could be clearly shown that PTR-MS was successfully implemented as a powerful bioprocess-monitoring tool. More than 20 VOCs show characteristic trends within E.coli fermentations. The VOCs are linked to host cell metabolism. Additional process variables like microarray data will gain insight into origin of VOC and the metabolic reactions involved.

On-line information on cell state via monitoring emitted volatiles opens promising perspectives of advanced process control regimes and accelerates the improvement of biotechnical production process.

References

[1] Luchner M., Gutmann R., Bayer K., Dunkl J., Hansel A., Herbig J., Singer W., Strobl F., Winkler K., Striedner G.: Implementation of proton transfer reaction-mass spectrometry (PTR-MS) for advanced bioprocess monitoring, Biotechnology and Bioengineering, 2012, online DOI: 10.1002/bit.24579

Analysis of breath gas biomarkers for medical applications - from laboratory based measurements to PoC monitoring

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Abstract

Analysis of volatile organic compounds (VOCs) in exhaled air offers optimal conditions for monitoring of physiological and pathophysiological processes in the whole body. Marker substances are produced at the cellular level, transported via the bloodstream and exhaled through the lungs without significant delay. Since there is no additional burden for the patient and no risk for the staff collecting the samples, breath analysis it optimally suited for screening purposes, and for repeated or continuous monitoring.

There is ample experimental and clinical evidence that volatile breath markers reflect a variety of metabolic, physiological and pathological biochemical processes such as dextrose or cholesterol metabolism, lipid peroxidation, oxidative stress, ischemia reperfusion injury, liver disease, renal failure, allograft rejection or lung injury. Even complex diseases like SIRS, sepsis, airway inflammation, cancer or obstructive sleep apnoea could be related to volatile biomarkers in the breath. Critically ill patients can be expected to exhale maximum concentrations of volatile markers since clinical conditions change rapidly and pathological conditions are profound in these patients.

Despite interesting diagnostic properties of some of these markers and despite its non-invasiveness, the analysis of volatile organic compounds in breath has not yet been introduced into clinical practice. Current problems to be solved include lack of knowledge on biomarkers and their exhalation kinetics and on confounding parameters. The latter may affect results and still hamper transformation of scientific data into clinical application. In addition, breath analysis still requires time consuming sample preparation, bulky equipment and excellent technical and analytical skills. A major part of the available data were obtained by means of sampling breath in bags or canisters, pre-concentration of large volumes, time consuming gas chromatographic (GC) separation and mass spectrometric (MS) detection.

During recent years smart combinations of techniques and progress in analytical instrumentation has been used to solve some of these problems. Automated sampling systems enable fast and reliable alveolar sampling. Improved (micro)extraction techniques for pre-concentration are requiring not more than a few cc of exhaled air for analysis down to the pptV level. Multidimensional and fast GC technology progressed in the way that miniaturized devices yield reliable substance separation within a few minutes. Modern mass spectrometry enables fast detection and substance identification on the pptV level. Fast and continuous monitoring of breath compounds without relevant delay can be done by means of PTR-MS.

Real time analysis by means of PTR-MS can enhance basic knowledge and understanding of breath biomarkers and can help to define potential applications in the field of medical breath

analysis. Prerequisite for quantitative VOC analysis from breath is the identification of the different phases of the respiratory cycle– e.g. the alveolar phase.
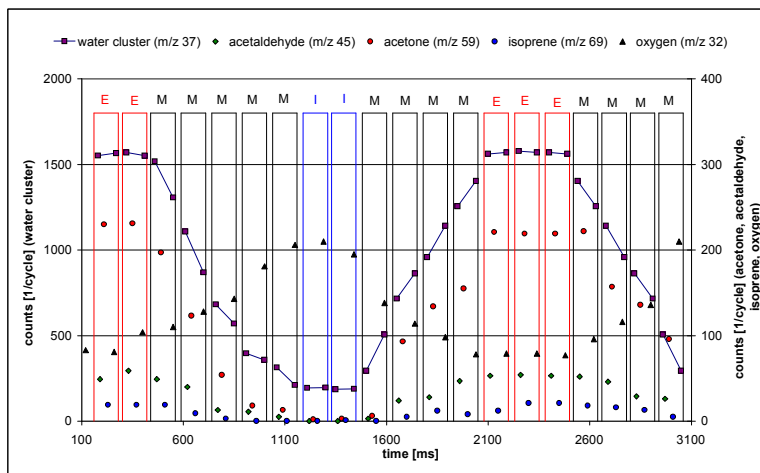
Fig. 1) PTR-MS signal assignment to different phases of the respiratory cycle.

Each box represents a single PTR-MSD measurement cycle. Signals within the black boxes (M) were assigned to mixed expiratory phases if the gradient between the first and the second water cluster signal was more than 2.5% [Δ (m/z = 37) > 2.5%]. Signals were attributed to alveolar phases (red boxes, E) if Δ (m/z = 37) < 2.5%, and when both signals were greater than the mean of the averaged water clusters. Blue boxes indicate cycles recognised as inspiratory phases (I). In these cases, values of both water cluster signals were less than the averaged signal and Δ (m/z = 37) < 2.5%.

If time resolutions <200 ms are used for PTR measurements phase assignment can be done by means of appropriate data algorithms.

Advances and limitations of real time PTR setup for biomarker identification and monitoring can be achieved by cross validation of PTR-MS with other techniques such as GC-MS and sensors.
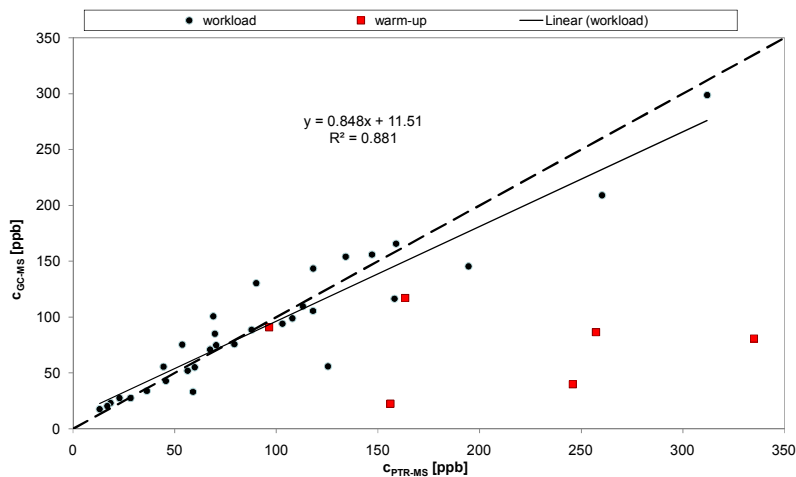
Fig 2) Correlation of PTR-MS and SPME-GC-MS data for isoprene during exercise in 6 volunteers

Most interesting aspects arise, when PTR-MS data and complementary data from other methods are combined in a clinical setup. Effects of pulmonary blood flow, distribution or ventilatory effects on the exhalation of VOCs can be addressed.
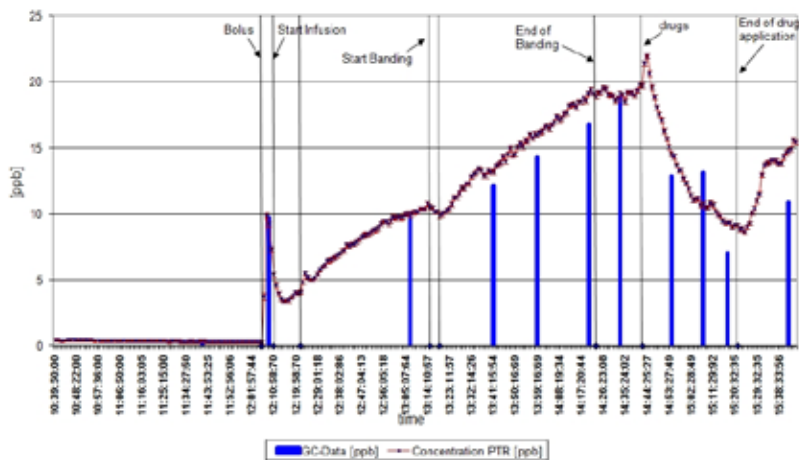
Fig 3) Real time (PTR-MS) monitoring of breath propofol in a acutely instrumented mechanically ventilated pig during reduction of blood flow (banding) and drug infusion [2]

Real time measurements can be used to enhance basic understanding of exhaled biomarkers and to realize metabolic monitoring or real time drug detection.
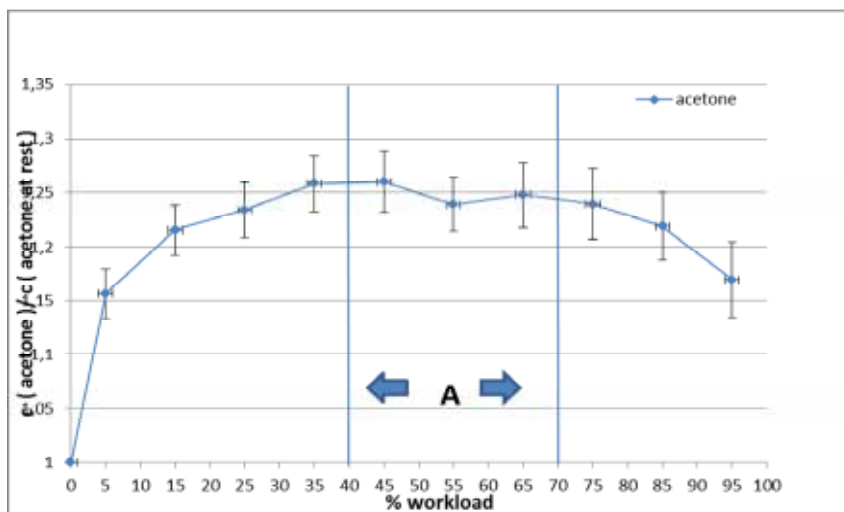
Fig 4: Normalized acetone concentrations (mean ± SEM) of 21 volunteers in relation to the relative workload (A= anaerobic trashold)

Real time monitoring by means of direct MS, enhanced separation and detection methods and bedside applicable detection techniques (e.g. sensors) will further promote scientific understanding as well as clinical application of breath analysis.

References

[1] Miekisch W, Schubert JK, Noeldge-Schomburg GFE. Diagnostic Potential of Breath Analysis - Focus on Volatile Organic Compounds. Clin Chim Acta 2004; 347:25-39.

[2] Miekisch W, Schubert JK. From highly sophisticated analytical techniques to life-saving diagnostics: Technical developments in breath analysis TrAC Trends in Analytical Chemistry 2006; 25: 665-673.

[3] Schwöbel HU, Schubert R, Sklorz M, Kischkel S, Zimmermann R, Schubert JK, Miekisch W. Phase resolved real-time breath analysis during exercise by means of smart processing of PTR-MS data. Anal Bioanal Chem. 2011; 401(7):2079-91.

[4] Kamysek S, Fuchs P, Schwoebel H, Roesner JP, Kischkel S, Wolter K, Loeseken C, Schubert JK, Miekisch W. Drug detection in breath: Effects of pulmonary blood flow and cardiac output on propofol exhalation. Anal Bioanal Chem. 2011;401(7):2093-102.

[5] Schubert R, Schwoebel H, Mau-Moeller A, Behrens M, Fuchs P, Sklorz M, Schubert JK, Bruhn S, Miekisch W. Metabolic monitoring and assessment of anaerobic threshold by means of breath biomarkers. Metabolomics 2012; DOI: 10.1007/s11306-012-0408-6.

Application of PTR-MS in mammalian cell culture

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Abstract

Mass spectrometry is a well-known technology to detect O_2 and CO_2 in the off-gas of cell culture fermentations. In contrast to classical spectrometers, the proton transfer reaction mass spectrometer (PTR-MS) applies a very soft ionization strategy and therefore the spectra show less fragments and are easier to interpret. In our study we applied the PTR-MS technology to monitor volatile organic compounds (VOC) in mammalian cell culture processes. Interesting masses were identified and correlations between PTR-MS data and off-line parameters will be presented.

Introduction

The PTR-MS technology has already been demonstrated to work sucessfully in microbial fermentations [1]. Hence it is only a small step to apply the device in field of mammalian fermentations. However, the equipment is quite similar there are several challenges to overcome such as lower flow rates and less biomass concentration.

Experimental Methods

A standard CHO cell culture process (batch and fed-batch) to produce a recombinant protein was choosen. The experiments were conducted in a modified 7L glass bioreactor. The duration of a cell culture fermentation was up to 16 day depending of the cultivation mode (batch or fed-batch).

Results

Several masses showed a distinguished trajectory such as an increase at a certain time point. As an example the mass 101 remained constant until the middle of the fermentation. After approximately five to six days the mass signal increased while the viability of the cell culture starts to decline.

Discussion

The PTR-MS showed the potential to gain insight in mammalian cell culture processes, though the meaning of the observed VOC's within in the metobolic pathways is still unknown.

References

[1] M. Luchner, R. Gutmann, K. Bayer, J. Dunkl, A. Hansel, J. Herbig, W. Singer, K. Winkler, G. Striedner, Implementation of proton transfer reaction-mass spectrometry (PTR-MS) for advanced bioprocess monitoring, Biotechnology and Bioengineering 109, 3059-3069, (2012)

Breath gas analysis in unrestrained mice: A survey of VOC screening using PTR-TOF 2000

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Abstract

The concept of breath gas analysis is based on the assumption that the concentration of exhaled volatile organic compounds (VOCs) correlates with the concentration of the circulating blood, and therefore the instantaneous status of metabolic pathways. The non-invasive access to and the measurement of exhaled VOCs by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) detect VOCs with high sensitivity in real-time and directly from the breath. Breath gas analysis in human (clinical) studies elucidated a high diagnostic potential. Though genetic mouse models for human disorders are of highest relevance in biomedical research, breath gas analysis has not yet been established in mice. The challenge was the adaption of PTR-MS towards a breath gas screen of unrestrained mice.

Recently we developed a prototype of a PTR-MS setup suitable for screening the exhaled VOCs of unrestrained mice for metabolic phenotyping of (mutant) mouse lines in the German Mouse Clinic. The novel method encompassed the repeated accumulation of the breath of an individual mouse and educed the source strength of exhaled VOCs. After the implementation of the new PTR-TOF2000-MS in the GMC/Metabolic screen the accumulation time of VOCs was reduced from 20 to about 5 minutes. Data analysis was highly automated especially regarding quality control, identification of confounders from urine, feces and adjusting for physical activity. The current measuring set-up and data processing was well suited for phenotyping and mid-term challenge experiments (days to weeks) in mice.

Standardized housing conditions, a defined genetic preposition to diseases and the possibility to investigate the interaction of lifestyle factors (e.g. nutrition, physical activity) and targeted metabolic alterations in established challenge experiments (fasting, experimental diets, glucose tolerance tests etc.) provide the possibility to decipher a VOC signature in mouse models of e.g. diabetes. First applications of VOC screening will be presented. In addition in first short-term challenge (<= 2 h) e.g oral / intraperitoneal glucose tolerance tests we identified the need of downscaling the accumulation time of breath gas to < 5 minutes. This requires the adjustment of the PTR-TOF-MS and data processing to the limit.

Applications in Food Science

10 years PTR-MS at FEM: from sensory analysis to omics

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Exactly 10 years ago appeared the first paper based on PTR-MS data acquired at FEM (at that time still named IASMA) [1]. Our goal was to evaluate a new, promising and rapid instrumental characterisation of food and to identify possible links with sensory analysis. The positive outcome of this study and the necessity to address other agri-food issues, led us to further investigate the potential of PTR-MS in food science and technology. Here, with the excuse to celebrate this tenth anniversary as well as the one of the PTR-MS conference, we would like to describe some milestones in the implementation of PTR-MS in food science and technology indicating at the same time prospectives and open problems. A more detailed discussion of our results, the difficulties that we encountered and a comparison of our ideas with the available literature can also be found in contributed papers presented at this conference[1-6,8-9].

We will start with the problem of semi-static sampling of food volatile compounds and with the possibility to implement advanced data analysis and data mining methods. In fact, it was questionable whether our idea to measure food samples enclosed in vials kept at constant temperature for a short time had some advantages compared to similar but more established methods (e.g. SPME-GC). It turned out that this method offers several advantages in terms of rapidity, sensitivity and reduction of artefacts while the impossibility, in general, to resolve the complex mixtures of volatile compounds in the head-space of food samples remains the main limitation[2]. This approach has been developed in parallel with other emerging direct methods in mass spectrometry (Ambient Mass Spectrometry) that have many similarities with PTR-MS from the applicative point of view as, for instance, the rapid and non-invasive measurement of intact samples. In this context, PTR-MS presents advantages (e.g. the possibility of quantification) and some obvious limitations (the possibility of measuring only volatile compounds).

The usefulness, or even the necessity in the case of PTR-ToF-MS, to apply multivariate statistical analysis and data mining was evident since the very first applications of PTR-MS for the rapid characterization of food products and will be shortly discussed also in relation with recent applications [2,3].

It is interesting to note that the methods developed, from sampling to data mining, make PTR-MS a valuable tool for metabolomics and for omics in general. In fact, as early as 2005, it was possible to identify by PTR-MS the first QTLs related to volatile compounds in apples that have been successively confirmed in a wider study[3]. A similar approach based on the new PTR-ToF-MS seems to be even more promising[3]. The potential of PTR-MS as an omic tool, nutrigenomics in this case, is confirmed also by our recent studies on the effect of diet and liver diseases on the breath of animal models and humans[4]. We also hope to be able to set models on the basis of PTR-MS data which will allow the prediction of sensory characteristics for large sample sets and thus open the way for a practical realisation of sensomic.

Of course, process monitoring is, also in the case of food science and technology, one of the best applications of PTR-MS. Perhaps nose-space measurements are the most vivid example[5,6] but

we can mention also the characterization of foods during shelf life or the monitoring of biological processes of technological relevance[7].

Based on these experiences, we started in 2010 a facility for the on-line monitoring of volatile compounds to foster collaborations with partners both external and at FEM that, in some cases, are not directly related with agroindustrial themes. Breath analysis both of animal models and humans[4] and the monitoring of plants for the production of bio-fuel[8] are recent examples of non-food applications. In this context, we try to develop new ideas to overcome the limitations of PTR-MS, to apply new methods (as the Switching Reagent Ion system by Ionicon)[2] and to study the fundamental aspects related to chemical ionization or to the determination of chemico-physical properties of volatile compounds[9]. We will conclude presenting the realisation of a prototype, after 10 years!, of our original proposal for a fully automated system, from sampling to data analysis and visualisation, that should make PTR-MS a real high-throughput technique and our activity, hopefully, more efficient.

References

[1] Biasioli, F., et al. Fingerprinting mass spectrometry by PTR-MS: heat treatment vs. pressure treatment of red orange juice - a case study (2003) Int J Mass Spectrom, 223 (1-3), 343-353

[2] Sanchez del Pulgar, J., et al. Rapid Characterization of Dry-Cured Ham Volatile Compound Profile by PTR-Tof-MS: Effect of Geographical Origin, Rearing System and Cross-Breeding. Oral communication. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[3] Cappellin, L., et al. Improved QTL analysis of apple volatile compounds by PTR-TOF-MS. Oral communication. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[4] Aprea, E., et al. Breath analysis on animal models and humans as a non invasive tool for studying liver diseases and their interaction with diet. Poster. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[5] Romano, A., et al. Hyphenation of PTR-ToF-MS and newly developed software provides a new effective tool for the study of inter-individual differences among tasters. Oral communication. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[6] Ting, V., et al. In-vivo volatile organic compound (VOC) release from fresh-cut apple cultivars: PTR-Quad-MS and PTR-ToF-MS. Poster. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[7] Tsevdou, M., et al. Monitoring and Modeling of Endogenous Flavour Compounds Evolution during Fermentation of Thermally, High Hydrostatic Pressure or Transglutaminase Treated Milk using PTR-TOF-MS (2013) Food Chemistry. In press.

[8] Papurello, D., et al. Proton Transfer Reaction-Mass Spectrometry (PTR-MS) as a rapid online tool for biogas VOCs monitoring in support of the development of Solid Oxide Fuel Cells (SOFCs). Poster. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

[9] Schuhfried, E., et al. Physico-Chemical Advances with PTR-MS . Poster. 6th International PTR-MS Conference. Universitätszentrum Obergurgl, Obergurgl – Austria. 3rd – 8th February 2013

Improved QTL analysis of apple volatile compounds by PTR-TOF-MS

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Abstract

In the modern definition of fruit quality, aroma is considered one of the main factors together with appearance, texture and nutritional properties [1]. The importance of aroma is due to its direct influence on the consumer appreciation, since a pleasant aromatic "bouquet" is a fundamental requirement for a high fruit quality standard.

The VOC set in apple is biochemically composed by major classes of compounds, such as alcohols, aldehydes, ketones, polypropanoids, sesquiterpens and esters [2]. The latter category (esters), in particular, is the most important class for apple, representing the major VOC class (~ 90%) produced during the apple fruit ripening process. The great impact that the aroma has on the apple fruit marketability, stimulated in the last decade the scientific community to gain knowledge about novel and valuable molecular markers associated with these traits. This became a main objective in order to facilitate apple breeding programs in the selection of the most favourable individuals.

In this context, a valuable approach is to identify Quantitative Trait Loci (QTL), thus determining links between genetics and fruit aroma in apple.

Dunemann and colleagues [2] carried out a comprehensive QTL mapping assay in apple, identifying QTLs associated to 20 major compounds (alcohols, esters and terpens), and located on 12 linkage groups, by using 150 seedlings of the cross 'Discovery x Prima' and a HS-SPME-GC detection equipment. Gas-chromatographic technique is, however, laborious and time consuming, limiting the aroma characterization of large apple collections, such as breeding material.

A valuable technological and analytical alternative is offered nowadays by techniques that privilege rapidity over analytical information, and have little sample preparation and no chromatography. The advantage is twofold: on the one hand a broader number of samples can be screened, on the other hand potential artefacts caused by extraction and concentration procedures are minimized [3]. A technique as such is represented by Proton Transfer Reaction - Mass Spectrometry (PTR-MS).

In this work the position of a set of QTL associated to VOCs was identified and validated in three different environments, where the progeny 'Fiesta x Discovery' was replicated (Wädenswil, Conthey and Cadenazzo), thus extending previous explorative studies [4].

Aroma emission profiles were characterized by a PTR-MS instrument. The QTL-VOC combined analysis performed among these three locations validated the presence of important QTL in genomic regions, two located in the linkage groups 2 and one in linkage group15, respectively, for compounds related to esters (m/z: 41, 43, 57, 61 and 131) and possibly to the hormone ethylene (m/z: 28). The

QTL set presented here confirmed that in apple some compounds are highly genetically regulated and stable across environments.

In a second study a modern PTR-MS coupled with a time-of-flight mass analyzer (PTR-TOF-MS) was employed for a combined QTL-VOC analysis on three different populations, encompassing hundreds of sibling samples. Given the higher resolution of PTR-TOF-MS compared to PTR-MS, the phenotypization of the apple siblings is strongly enhanced, entangling hundreds of peaks for which a sum formula could be assigned [5, 6]. In many cases also the underlying compound could be determined, thanks to targeted analyses carried on on a limited number of samples using SPME/GC-MS [7, 8]. A very large number of QTL could be identified, going far beyond the confirmation of the QTL found in the first study by PTR-MS. Such QTL were associated to several classes of VOCs constituting the apple aroma profile. The statistical significance of the QTL was also extremely enhanced, reflecting the better phenotypization of the samples provided by PTR-TOF-MS. Employing PTR-TOF-MS therefore represented a major breakthrough in addressing this important problem.

We also devoted a strong effort to automatize the whole combined QTL-VOC analysis process by writing specific routines in MATLAB (MathWorks, Natick, USA) and R (R Foundation for Statistical Computing, Vienna, Austria) which allow studying very large populations with a sustainable effort.

In general, these findings can be of outmost importance in ongoing breeding programs.

References

[1] M.C. Bourne, Food texture and viscosity: concept and measurement., Academic Press, New York State Agricultural Experiment Station, Institute of Food   Science, Cornell University, Geneva, New York, USA., 2002.

[2] F. Dunemann, D. Ulrich, A. Boudichevskaia, C. Grafe, W.E. Weber, QTL mapping of aroma compounds analysed by headspace solid-phase   microextraction gas chromatography in the apple progeny «Discovery» x «Prima», Mol. Breed. 23 (2009) 501–521.

[3] J. Han, R. Datla, S. Chan, C.H. Borchers, Mass spectrometry-based technologies for high-throughput metabolomics, Bioanalysis. 1 (2009) 1665–1684.

[4] E. Zini, F. Biasioli, F. Gasperi, D. Mott, E. Aprea, T.D. Märk, et al., QTL mapping of volatile compounds in ripe apples detected by proton transfer reaction-mass spectrometry, Euphytica. 145 (2005) 269–279.

[5] C. Soukoulis, L. Cappellin, E. Aprea, F. Costa, R. Viola, T.D. Märk, et al., PTR-ToF-MS, A Novel, Rapid, High Sensitivity and Non-Invasive Tool to Monitor Volatile Compound Release During Fruit Post-Harvest Storage: The Case Study of Apple Ripening, Food and Bioprocess Technology. (2012).

[6] L. Cappellin, F. Biasioli, P.M. Granitto, E. Schuhfried, C. Soukoulis, F. Costa, et al., On data analysis in PTR-TOF-MS: From raw spectra to data mining, Sensors and Actuators B-Chemical. 155 (2011) 183–190.

[7] L. Cappellin, E. Aprea, P. Granitto, R. Wehrens, C. Soukoulis, R. Viola, et al., Linking GC-MS and PTR-TOF-MS fingerprints of food samples, Chemometrics and Intelligent Laboratory Systems. 118 (2012) 301–307.

[8] L. Cappellin, C. Soukoulis, E. Aprea, P. Granitto, N. Dallabetta, F. Costa, et al., PTR-ToF-MS and data mining methods: a new tool for fruit metabolomics, Metabolomics. 8 (2012).

Food oral processing understanding, a way to revisit the sensory properties of food

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Abstract

In humans food oral processing is the first step in the digestive process. It prepares the food to be swallowed and then to undergo the process of digestion. During chewing, the food is deconstructed by the combined action of chewing and saliva to form a bolus. The particle size of the bolus is reduced and the saliva is continuously produced by the salivary glands for humidifying and impregnating the food. Saliva helps the breakdown of the food with enzymes it contains. It can at least partially dissolve and release different compounds from the food matrix such as aroma, taste and nutrients compounds. It impregnates and lubricates the bowl and also allows cohesion of the particles to prepare the step of swallowing. The compounds responsible for the flavor of food are released during this complex process leading to the perception of the food sensory properties and contributing significantly to the acceptability of the product by the consumer. Understanding this process of food breakdown and bolus formation appears thus as a way to revisit food functional properties. In this talk, we propose to review through chosen examples the major mechanical, physico-chemical and biochemical phenomena that held in the mouth during chewing of food and their impact on the sensory properties of food. The large interindividual variability observed on these phenomena among the population will be particularly emphasized.

Introduction

In humans, orality combines all the functions of the orofacial sphere (in which the mouth is the key organ) i.e. ventilation, expression, food breakdown, and sensory perception. The mouth is the first organ to perceive food and the different signaling events associated to food breakdown [1]. The release of sensory stimuli, major contributors to our preferences and rejections, also occurs within the mouth (Figure 1). These events are extremely complex and, as such, their description necessitates to combine many variables coming from different disciplines i.e. physics, chemistry, physiology, rheology, psychology, behavioral science, food science.

Two main mechanisms are involved in the process of food breakdown in the mouth, i.e. mastication and salivation. Mastication can change the mechanical properties of solid food so that it can be swallowed. The breakdown of the food is mainly influenced by its composition and texture, hard and dry food demanding of many chewing cycles and works to be fragmented into particles and impregnated with saliva before being swallowed [2]. In fact, to be swallowed, the bowl must reach a certain level of comminution (particle size) and a certain level of lubrication depending on the incorporation of saliva. Saliva interacts with the bolus during its formation during the process of mastication. Studies on the incorporation of saliva during chewing showed some rates of hydration of bolus up to 80% depending on the matrices and subjects considered [3, 4]. Food oral processing leads thus to a product far from

what is originally put in the mouth and therefore impacts directly on the dynamics of release of active substances and the delivery of their functionality (sensory, nutritional etc ...).
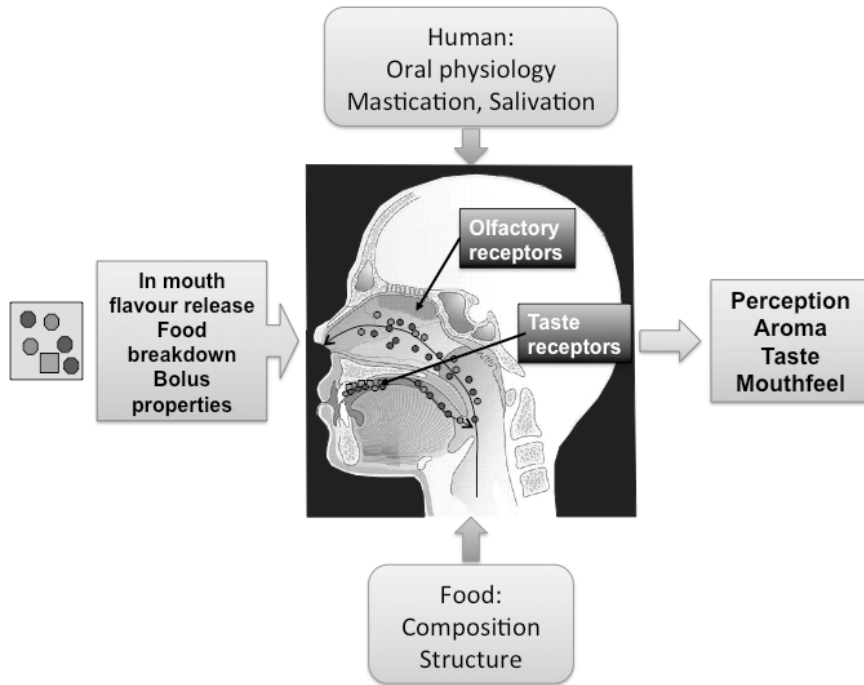
Figure 1: schematic representation of oral food breakdown leading to the release and perception of taste and aroma.

Understanding food flavour through food oral processing

Aroma release and perception

Retro-nasal olfaction of aroma, which occurs in humans while eating food, is a key factor driving food perception, acceptability and intake. However, its mechanism is poorly understood. One central question arises from the repeated observation of considerable inter-individual variability in the amount of aroma compounds recorded at the nostril using API-MS or PTR-MS during food consumption [5, 6]. The origin of this variability has not been satisfactorily explained. Recent reports have indicated that the consumption of the same amount of product in the mouth can produce a 10-fold range of variation in the amount of aroma compound released in breath at the nostril level [7]. The results of these studies ultimately suggest that chewing behavior during mastication and swallowing contribute to inter-individual variations in the transfer of aroma compounds from the product to the oral cavity and then to the nasal cavity. Different mechanisms may explain the reportedly marked inter-individual variations in aroma release profiles. In particular, the inter-individual differences in tongue movements observed during swallowing may generate different patterns of aromatized air passage through the velum and result in the different aroma profiles observed at the nostril level. Very recently, it has been observed that differences in aroma profile were in large part due to differences in changes of the oral cavity volume after

deglutition in humans and that these volume changes thus appear to be a fundamental, individual physiological parameter that explains in-nose aroma release variations in humans [8]. However, these differences depend on the structure and composition of the product but also on the nature of the aroma compounds in the food matrix [9].

Salt and saltiness

Usually the saltiness is related strongly to salt levels in food. However this phenomenon was principally observed for high amount of salt. Various composition and structure factors of the product can influence the release of sodium in the mouth and thus may modulate the perception of salt [10]. The kinetics of release of sodium in the mouth during chewing of food show also significant differences between individuals that are partly explained by chewing behaviour and physiological characteristics of consumers [11]. It was also observed relationships between salt content in cheese, aroma and salt release and perception. However, little is known about the relationship between salt release and perception in the mouth and the oral consumer physiological characteristics. In this context, recent works conducted in our research team on cheese matrix showed that the different oral physiological parameters that could explain salt perception differ in function of the level of salt in the matrix. In particular, for high salt cheeses, saltiness is correlated only with Na+ amount in the saliva while for low salt cheeses, saltiness depends on saliva composition but also on masticatory performance of the individuals [12].

Fat and fattiness

In humans, the perception of fat in food is a complex process involving many sensory modalities (texture, aroma and flavour). For solids and semi-solid fatty matrices, saliva and the shear forces applied during mastication contribute to their breakdown and/or destabilisation in emulsified systems [13]. These mechanisms are often dependent on the fat content of the food and thus play an important role in not only the perception of texture but also the release of compounds responsible for the flavour of "fat" [14]. In addition, saliva is directly involved in the orosensory detection of dietary fat and their hydrolysis products, i.e., free fatty acids, which occurs at different detection levels, i.e., taste and multimodal [15]. Interestingly, the involvement of some of salivary variables in the perceived intensity and preference towards oil emulsions was also shown [16]. In addition to detection, these mouth processes also contribute greatly to a preference for or rejection of fat. Preferences are related to not only the perception of texture but also gustatory and olfactory components of fat [17].

Conclusion

This review has been aimed to show the important part of mastication and salivation on the disintegration of the bowl and the release of aroma and taste substances. One of the main conclusions in all studies conducted on chewing and salivation and on a significant number of human subjects is the extreme interindividual variability observed. Conversely, more studies highlight the stability and reproducibility of individual oral and salivary characteristics. One of the scientific challenges for future research in this area will be to establish the causal links between interindividual oral physiological variability and those observed in the sensory perception of food.

References

[1] C. Salles, M.-C. Chagnon, G. Feron, E. Guichard, H. Laboure, M. Morzel, E. Sémon, A. Tarrega, C. Yven, In-mouth mechanisms leading to flavor release and perception, Crit. Rev. Food Sci. Nutr., 51, 67-90 (2011).

[2] E. Guichard, M. Repoux, E. Semon, H. Laboure, C. Yven, G. Feron, Understanding the dynamics of flavour compounds release during food mastication of cheese products in function of oral physiology, in: The 9th Wartburg Symposium on Flavour Chemistry and Biology, Eisenach (GER), (2010).

[3] C. Yven, J. Patarin, A. Magnin, H. Labouré, M. Repoux, E. Guichard, G. Feron, Consequences of individual chewing strategies on bolus rheological properties at the swallowing threshold, J. Texture Stud., 43, 309-318 (2012).

[4] M.B. Gaviao, A. van der Bilt, Salivary secretion and chewing: stimulatory effects from artificial and natural foods, Journal of Applied Oral Science, 12, 159-163 (2004).

[5] E. Pionnier, J.-L. Le Quéré, C. Salles, Real time release of flavor compounds and flavor perception. An application to cheese, in: A.M. Spanier, F. Shahidi, T.H. Parliment, C. Mussinan, C.T. Ho, E. Tratras Contis (Eds.) The 11th International Flavor Conference: Recent advances in food flavor, The Royal Society of Chemistry, Cambridge 2005, Samos (GRC), pp. 13-22, (2004).

[6] I. Gierczynski, H. Laboure, E. Guichard, In vivo aroma release of milk gels of different hardnesses: Inter-individual differences and their consequences on aroma perception, J. Agric. Food Chem., 56, 1697-1703 (2008).

[7] M. Repoux, E. Sémon, G. Feron, E. Guichard, H. Labouré, Inter-individual variability in aroma release during sweet mint consumption, Flavour Fragr. J., 27, 40-46 (2012).

[8] A. Mishellany-Dutour, A. Woda, H. Labouré, P. Bourdiol, P. Lachaze, E. Guichard, G. Feron, Retro-nasal aroma release is correlated with variations in the in-mouth air cavity volume after empty deglutition, PLoS One, 7, e41276 (2012).

[9] I. Gierczynski, E. Guichard, H. Labouré, Aroma perception in dairy products: the roles of texture, aroma release and consumer physiology. A review, Flavour Fragr. J., 26, 141-152 (2011).

[10] V.A. Phan, C. Yven, G. Lawrence, C. Chabanet, J.-M. Reparet, C. Salles, In vivo sodium release related to salty perception during eating model cheeses of different textures, International Dairy Journal, 18, 956-963 (2008).

[11] G. Lawrence, C. Septier, C. Achilleos, P. Courcoux, C. Salles, In vivo sodium release and saltiness perception in solid lipoprotein matrices. 2. Impact of oral parameters, J. Agric. Food Chem., 60, 5299–5306 (2012).

[12] C. Septier, A. Saint-Eve, M. Repoux, C. Vergoignan, C. Salles, G. Feron, Can saliva composition explain salt perception in cheese?, in: International Conference on Food Oral Processing - Physics, Physiology and Psychology of Eating, Leeds (UK), pp. 1 p., (2010).

[13] D.M. Dresselhuis, E.H.A. de Hoog, M.A. Cohen Stuart, M.H. Vingerhoeds, G.A. van Aken, The occurrence of in-mouth coalescence of emulsion droplets in relation to perception of fat, Food Hydrocolloids, 22, 1170-1183 (2008).

[14] G. Feron, E. Guichard, Lipides et arômes: rôles dans la perception de la flaveur et du gras chez l'homme, Innovations Agronomiques, 10, 69-80 (2010).

[15] J. Poette, J. Mekoué, C. Genot, E. Neyraud, O. Berdeaux, A. Renault, E. Guichard, G. Feron, Fat sensitivity in human: possible relationships with oral and saliva characteristics., Submitted, (2012).

[16] E. Neyraud, O. Palicki, C. Schwartz, S. Nicklaus, G. Feron, Variability of human saliva composition: Possible relationships with fat perception and liking, Arch. Oral Biol., 57, 556-566 (2012).

[17] G. Feron, J. Poette, In-mouth mechanism leading to the perception of fat in humans: from detection to preferences. The particular role of saliva, Oléagineux, Corps gras, Lipides, In Press, (2012).

Modifying PTR-MS operating conditions to analyze high ethanol containing samples: Application to spirit characterization from dynamic flavor releases during consumption.

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Abstract

The analysis of high ethanol containing samples with Proton Transfer Reaction Mass Spectrometry (PTR-MS) raises the problem of the modification of ionization conditions within the drift tube, which could result in primary ion depletion. In this paper, we proposed of a new and reliable method for *in vitro* and direct *in vivo* analysis of aroma release from high ethanol containing beverages using PTR-MS without any modification of the PTR-MS system. By optimizing some PTR-MS parameters such as the inlet flow and the drift tube parameters, the stability of the ion source signal can be controlled, providing stable analytical conditions. This approach was applied to characterize and discriminate brandies of different qualities according to their dynamic aroma release profile. Results showed that new drift tube parameters enable to have a quantitative and qualitative discrimination between different spirits using ion release kinetic parameters. This new simple method can be applied to gain insight into the effect of alcoholic beverage characteristics on aroma release and thus better understand the origin of perception differences depending on product quality.

Introduction

In recent years, consumers have become much more demanding concerning food quality. When alcoholic beverages such as wine and spirits are concerned, their quality is often related to aromatic richness and complexity and the sensory importance of retro-olfactory perception has been demonstrated in numerous studies [1, 2]. In the last decade, many efforts have been made to understand the dynamic dimension of sensory perception [3, 4, 5]. To better understand relationships between aroma perception and release, analytical techniques such as PTR-MS or APCI-MS constitute useful tools and are more and more used. But in the case of PTR-MS analysis of ethanol containing samples, the presence of ethanol completely changes ionization conditions within the drift tube, by notably depleting H_3O^+ primary ions. Several studies showed that ethanol limit concentration under which this phenomenon was not observed was about 100 parts per million by volume (ppmv) in the sample headspace or 4 % v / v in the solution [6, 7, 8]. Different experimental set-ups were developed to overcome this problem, mainly base on sample dilution, which can constitute a drawback for detecting molecules present at very low concentration [6, 9]. In addition, these methods appeared to be

difficult to apply for in vivo analysis. The aim of the present study was to find appropriate operating conditions for the analysis of high ethanol content samples and which could be applied for both in vitro and in vivo analysis. The in vivo approach was used to validate that the PTR-MS sensitivity with optimized operating conditions was sufficient to characterize and to compare different brandies.

Experimental Methods

Three commercial brandies, all containing 40 % v/v of ethanol but varying in aging and thus in quality, were chosen for this study. Data were collected using a High Sensitivity Proton Transfer Reaction - Mass Spectrometer (Ionicon Analytik, Innsbruck, Austria). The first part of the study concerned parameter optimization. PTR-MS drift tube parameters Udrift, pdrift and Tdrift were varying according to a complete experimental design and where applied to in vivo and in vitro approaches. Combinations were chosen to screen E/N from above 70 Td to 700 Td. In vivo analysis was then performed with a panel of 11 persons, which were asked to consume 5mL of brandies. Measurements were performed using the optimized values of parameters previously selected.

Results

Among all combinations tested during the first part of the study, optimized conditions selected were pdrift = 0,8 mbar, Udrift = 800V and Tdrift = 60°C (E/N = 483 Td) for the in vitro approach (brandies headspaces) and pdrift = 1,2 mbar, Udrift = 500V and Tdrift = 60°C (E/N = 201 Td) for in vivo conditions. These conditions were selected so that the depletion of the H_3O^+ primary ion intensity remained lower than 5% and the ethanol ion (m/z 47) signal did not exceed 10% of the H_3O^+ primary ion (m/z 19) signal [9]. We also checked that the intensity of ion m/z 37 (related to water clusters) represented less than 2% of the total signal intensity (limitation due to the formation of water clusters which can modify the initial protonation reaction). In vivo conditions were then applied to characterize aroma release from brandies and highlighted differences depending on product quality. The quantity of VOCs released generally increased with the aging of the spirits. The main difference between the two old and high quality brandies and the young brandy mainly concerned ions issued from esters ions.

Discussion

By selecting appropriate values for drift tube parameters, we managed to control the level of ethanol transmitted to the drift tube and thus to ensure the stability of H_3O^+ primary ion signal. Drift tube parameters have to be adjusted depending on the amounts of ethanol transmitted to the PTR-MS in order to optimize VOC detection and to avoid humidity problems. One of the advantages of the proposed method is that no system modification is required. Its application for in vivo analysis showed that, despite an important inter-individual variability, optimized analysis conditions enabled a correct discrimination of the 3 brandies by highlighting differences between ions on their release behaviors during consumption. This new simple method can be applied to gain insight into the effect of alcoholic beverage characteristics on aroma release and perception in relation with raw material quality, processing and their typicality.

References

[1] Buettner, A., Koot, A., Akkermans, W., Araghipour, N., Rozijn, M., Baltussen, M., Wisthaler, A., Märk, T. and Frankhuizen, R., Butter and butter oil classification by PTR-MS, European Food Research and Technology, 227, 307-317 (2008).

[2] Genovese, A., Piombino, P., Gambuti, A. Moio, L., Simulation of retronasal aroma of white and red wine in a model mouth system, Investigating the influence of saliva on volatile compound concentrations, Food Chemistry, 114, 100-107 (2009).

[3] Meillon, S., Urbano, C., Schlich, P., Contribution of the Temporal Dominance of Sensations (TDS) method to the sensory description of subtle differences in partially dealcoholized red wines, Food Quality and Preference, Vol. 20, Issue 7, 490-499 (2009).

[4] Meillon, S., Viala, D., Medel, M., Urbano, C., Guillot, G., Schlich, P., Impact of partial alcohol reduction in Syrah wine on perceived complexity and temporality of sensations and link with preference, Food Quality and Preference, Vol. 21, Issue 7, 732-740 (2010).

[5] Déléris, I., Saint Eve, A., Guo, Y., Lieben, P., Cypriani, M. L., Jacquet, N., Brunerie, P., Souchon, I., Impact of Swallowing on the Dynamics of Aroma Release and Perception during the Consumption of Alcoholic Beverages, Chemical Senses, Vol. 36, Issue 8, 701-713 (2011).

[6] Boscaini, E., Mikoviny, T., Wisthaler, A., Hartungen, E. V., Mark, T. D., Characterization of wine with PTR-MS, International Journal of Mass Spectrometry, 239, 215-219 (2004).

[7] Aznar, M., Tsachaki, M., Linforth, R. S. T., Ferreira, V., Taylor, A. J., Headspace analysis of volatile organic compounds from ethanolic systems by direct APCI-MS, International Journal of Mass Spectrometry, 239, 17-25 (2004).

[8] Tsachaki, M., Linforth, R. S. T., Taylor, A. J., Dynamic Headspace Analysis of the Release of Volatile Organic Compounds from Ethanolic Systems by Direct APCI-MS, Journal of Agricultural and Food Chemistry, 53, 8328-8333 (2005).

[9] Spitaler, R., Araghipour, N., Mikoviny, T., Wisthaler, A., PTR-MS in enology: Advances in analytics and data analysis, International Journal of Mass Spectrometry, 266, 1-7 (2007).

Predicting the Sensory Profiles of Coffee based on PTR-ToF-MS and GC-MS Measurements

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Abstract

An analytical tool to predict the flavor profile of coffee was developed based on measurements of the headspace of coffee with proton transfer reaction time of flight mass spectrometry and solid phase micro extraction gas chromatography coupled to mass spectrometry and correlating the instrumental data to sensory profiles by an expert panel. Sensory evaluation comprised the taste attributes acidity and bitterness, the tactile impression body, the flavor attributes roasty, flowery/fruity, cereal, chocolate, herbal, and spicy. These nine sensory markers were combined with either 78 chemical markers of the HS PTR-ToF-MS analysis or 16 chemical markers of the HS SPME GC/MS analysis in a partial least squares analysis, resulting in a predictive model for the flavor profile of a cup of coffee. The predictive model was successfully validated on four additional coffee samples, using instrumental data from HS PTR-ToF-MS and HS SPME GC/MS.

Introduction

Reflecting on the incredible rise of coffee over the past two centuries to one of the most consumed beverage worldwide, many economic, social and cultural factors as well as the stimulating effect of caffeine have been put forward. But there is no doubt that the unique aroma and taste (its flavor) has also been a major driver in this ongoing success story of coffee. Hence one question that has intrigued generations of flavor scientists is whether the perceived flavor of coffee can be measured and predicted based on its chemical and physical properties.

In this article we outline a strategy and discuss a practical application of such a predictive model. The model builds on a stepwise process introduced in a former publication [1], which was further developed and refined for this work. The approach used here is schematically outlined in Fig. 1.

In a first phase (data acquisition), a series of coffee samples are measured by instrumental means as well as profiled by a sensory panel. Here it is important to consider two points, critical to the quality of the predictive model: (i) one should include a large number of coffee samples and cover a large and significant sensory space; (ii) each sample should be measured in at least three repetitions, in order to calculate uncertainties for each predicted sensory attribute.

In a second phase (model development) multivariate statistical techniques are used to develop a mathematical model that links instrumental data with individual sensory attributes.

In the final, third phase (validation) a new set of coffee samples is measured by the instrumental technique and the predicted sensory profiles (via the mathematical model developed in phase 2) are compared to the sensory profiles established by the expert sensory panel. The smaller the statistical uncertainty of each value and the better the overlap between both dataset, the more accurate is the predictive model and the higher is its quality.
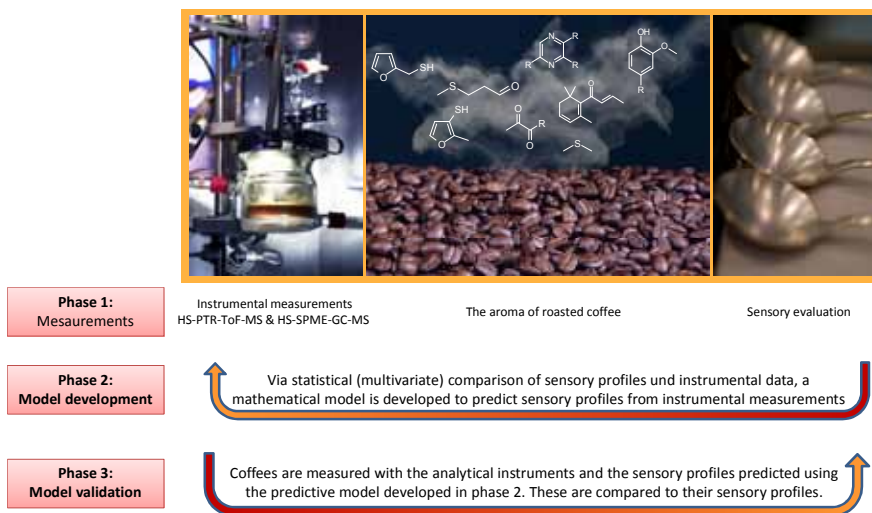
Figure 1: Schematic representation of the three phases in developing the predictive model [2].

In this study, 16 different coffees from the Swiss market were analyzed by Headspace Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (HS PTR-ToF-MS) and by Headspace Solid-Phase-Micro-Extraction Gas-Chromatography Mass Spectrometry (HS SPME GC/MS). In parallel, the same coffees were profiles by a trained sensory panel. Based on this dataset, a predictive model was developed, which was subsequently validated based on four new coffees.

Experimental Methods

Coffee Brew Preparation

20 different coffees were provided by local roasters or bought in local supermarkets. Coffee brew was prepared by French Press extraction. 60 g of freshly ground coffee (espresso grinder KED 640, Ditting, Switzerland, grinding degree 8 = coarse) was extracted with 1000 ml of hot water at 90°C for 4 minutes (4°dH, Brita filtered, Switzerland). This same coffee preparation procedure was used for instrumental and sensory analysis. For instrumental analysis, the brew was filled in a headspace vial (10 ml for HS SPME GC/MS, 20 ml for HS PTR-ToF-MS) and analyzed immediately with HS SPME GC/MS and HS PTR-ToF-MS.

HS SPME GC/MS Analysis

The composition of the VOC in the HS of the coffee brew was analyzed with HS SPME GC/MS. A polydimethylsiloxane/ divinylbenzene (PDMS/DVB) SPME fiber (65 μm film thickness, Supelco, Sigma-Aldrich Chemie GmbH, Switzerland) and a DB-WAX column (30 m x 250 μm x 0.25 μm, Agilent Technologies, Switzerland) were used. *SPME parameters* (Gerstel, Switzerland) were as follows. Incubation: 4 min at 50 °C with agitating at 250 rpm; Extraction time: 7 min at 50 °C; Desorption time: 5 min at 240 °C; GC/MS parameters (7890/5975N, Agilent Technologies, Switzerland): 35 °C for 1 min; then 4 °C/min to 100 °C for 10 min; then 30 °C/min to 130 °C for 8 min; then 6 °C/min to 220 °C for 5 min; in splitless mode; flow 1 mL/min; EI source 70 eV, 230 °C; detector 150 °C. For data analysis, the software MSD Chemstation (Version G1701 EA E.02.00.493, Agilent Technologies, Switzerland) and the database NIST08

was used. Chemical identification was performed via the respective mass spectrum and the retention time. 16 out of 126 identified molecules were chosen for the model, based on their significance regarding the difference between the coffee brews, their intensity in the headspace, their standard deviation as well as their aroma. All measurements were performed in triplicate.

HS PTR-ToF-MS Analysis

The PTR-MS analysis (PTR-ToF-MS 8000, Ionicon Analytik GmbH, Austria) was performed in a double jacketed glass vial thermostated at 50 °C (C25/F5, Haake, Switzerland), mounted in an oven (FD 53, Binder, Switzerland) which was held at 60 °C (see left frame of Fig. 1). A constant flow of air (450 ml/min) was flushing the headspace of the brew, and subsequently diluted with filtered air (4 L/min) before being analyzed with the PTR-ToF-MS (inlet flow: 200 ml/min, inlet and drift tube temperature: 70 °C). The signal was monitored for circa 5 min. For data analysis, an average over 100 s of the respective signal intensity was used. 16 out of 94 identified molecules were chosen for the predictive model, based on their significance regarding the difference in the coffee brews, their intensity in the headspace and their standard deviation. All measurements were performed in triplicate.

Sensory Evaluation

The sensory attributes acidity, bitterness, body, roasty, flowery/fruity, cereal, chocolate, herbal, and spicy were scored on a range from 1 (very low) to 10 (very high) by a panel consisting of three experts. All measurements were performed in triplicate, amounting to nine profiles per samples. The sensory profiles subjected to the statistical analysis were the average of all nine, with the uncertainty for each attribute and sample at 95 % confidence interval.

Statistical Data Analysis

The statistical data evaluation was performed as described elsewhere [1]. In short, the analytical data were scaled by the mean value of a marker molecule over all coffee samples as well as by the mean value of all markers for one coffee sample before being z-transformed, the sensory data were scaled by the mean value of all markers for one coffee sample before being z-transformed. For the partial least squares analysis (NCSS 2007, Hintze, J. NCSS, PASS, and GESS; NCSS: Kaysville, Utah, 2006), the principal component analysis of the analytical data was projected onto the principal component analysis of the sensory data. The predictive model was established with 16 coffees, the validation of the model was performed using four additional coffees.

Results and Discussion

The statistical analysis of the sensory data revealed that the coffees can be grouped into four families. The characteristics of the respective families are: *Family 1*: bitter, roasty, weak in acidity and flowery/fruity. *Family 2:* cereal. *Family 3:* herbal. *Family 4:* flowery/fruity, acidity. By using partial least squares analysis, the sensory data were well predicted both by HS PTR-ToF-MS data (Fig. 3a) and HS SPME GC/MS data (Fig. 3b). In general it can be observed that a very high fit is achieved between the predicted and actual sensory profiles. A closed look at the results revealed: (i) Best results were achieved for the prediction of the attributes acidity, bitterness, roasty and chocolate. (ii) The 16 coffee samples covered a large range in the sensory scores, establishing a good base for a predictive model with respect to these attributes. (iii) From a statistical perspective, the attributes body, cereal and spicy were predicted quite accurately as well. Yet, considering that the spread in the sensory scores for the 16 coffees was rather small for these attributes, the model has a lower predictive power. (iv) For the two attributes flowery/fruity and herbal the prediction was of lower quality, most probably due to the lack of analytical markers and possibly also due to less precise definition of the sensory attribute (e.g. flowery/fruity).
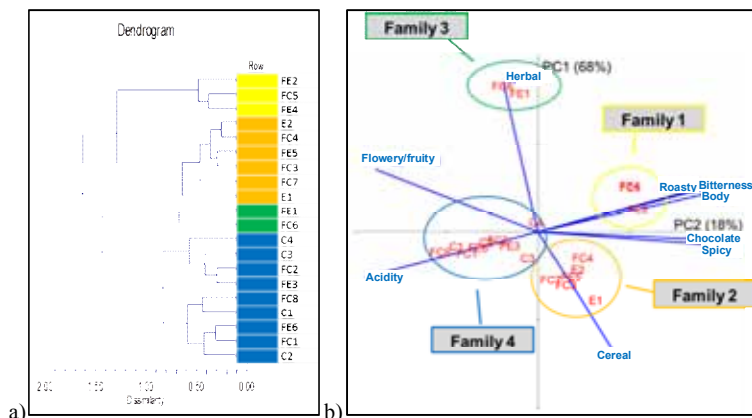
Figure 2: a) Cluster analysis of sensory data. b) Principal component analysis of sensory data and grouping in four families. Each coffee is labeled by a two or three digit code. F: "Fair Trade" coffee; E: espresso blend; C: blend for a long cup (lungo).
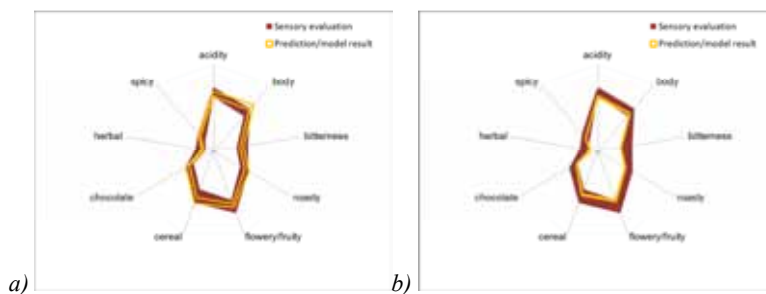
Figure 3: Sensory evaluation of the flavor profile of coffee brew (brown curve) in comparison with predicted profile (orange), based on a) HS PTR-ToF-MS and b) HS SPME GC/MS. The width of the curves corresponds to the standard deviation.

In conclusion, the sensory profile of a cup of coffee can be predicted both by HS PTR-ToF-MS and HS SPME GC/MS. Yet it should be stressed that one can only expect accurate results within the sensory space covered by the 16 coffees used for deriving the model. Hence, in order to improve the predictive model, a larger database (i.e. more coffees) that covers the largest possible range for each sensory score would be valuable. We are currently conducting a follow-up study with more that forty coffee samples and a large variability in the sensory profile, with the aim to further improve the quality of the predictive model.

References

[1] C. Lindinger, D. Labbe, P. Pollien, A. Rytz, M. A. Juillerat, C. Yeretzian, I. Blank, When Machine Tastes Coffee: Instrumental Approach To Predict the Sensory Profile of Espresso Coffee Anal.Chem. 80, 1574-1581, (2008).

[2] Christian Lindinger, Chahan Yeretzian, Imre Blank; When Machine Tastes Coffee: Successful Prediction of Coffee Sensory Profiles by Instrumental Methods Based on On-line PTR-MS; CHIMIA 63(5), 292 (2009)

Can PTR-MS be used for fast measurement of rancid flavour of milk?

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Abstract

Milk is very vulnerable to off-flavour. Especially lipolysis can accumulate low boiling free fatty acids which can give rise to a rancid flavour in milk. Harsh and wrong mechanical treatment of milk in modern farming with e.g. automatic milking increase the content of free fatty acids in milk. Individual free fatty acids are normally quantified by GC-MS, but the short-chain free fatty acids – especially butyric acid (C4) – are due to high volatility difficult to measure accurately. In many dairies, a measurement based on infrared analysis is used for fast analysis of the milk composition at arrival and the newest versions of the instruments have a calibration for total free fatty acids as well. However, the amount of total free fatty acids is not always correlated to rancid flavour.

The hypothesis of this research is that PTR-MS can be used as a fast method for analysis of individual free fatty acids in milk exploiting the high volatility of the short-chain free fatty acids. The volatility of these is dependent on pH of the solution and temperature, as lower pH and higher temperature gives higher volatility. However, this is not straight-forward when applied to milk. Even though milk might seem as a simple product to the consumer, this is not the case in the laboratory, as pH and temperature have a large impact on the colloid stability of milk and, in addition, milk is a product with high natural variability in composition. A pH of 4.6 induces coagulation, and likewise high temperatures induce changes in the proteins such as denaturation. Furthermore, binding of the volatile compounds to the milk proteins is not completely understood. In this study, the effect of pH and temperature on the release of butyric acid in milk was investigated using PTR-MS and the results were compared with the estimated equilibrium concentration in the headspace.

Hyphenation of PTR-ToF-MS and newly developed software provides a new effective tool for the study of inter-individual differences among tasters

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Abstract

PTR-ToF-MS was applied with the aim to study inter-individual differences in the experience of coffee tasting by means of nosespace analysis. Data analysis was greatly simplified by the employment of in-house developed software tools, some of which were tailored to nosespace analysis. Reproducible differences between tasters were observed in terms of the release profiles of selected volatiles. The overall results showed that the integration of high-performance instrumental techniques with powerful data processing tools allows for more rapid and effective data exploitation in the field of nosespace analysis.

Introduction

The determination of sensorial characteristics represents -for foods and beverages- an element of paramount importance in the global evaluation of the product. In most sensory studies the attention of the panel leader is turned towards the assessment of the product, with tasters being regarded as the "analytical tools" that make this assessment possible. Less attention is instead paid to the evaluation of tasters themselves. This is somewhat surprising, especially given the fact that in humans the inter-individual variability that characterizes the olfactory capability appears to be considerably larger than what is observed for other senses [1].

PTR-MS has successfully been applied to the real-time characterization of flavour release during food consumption, also referred to as nosespace [2]. Due to higher mass and time resolution, ToF mass analyzers provide an enhancement of the capabilities of nosespace. The large amounts of data thus generated (roughly 10^8 single values can be produced during a three-minute session) paradoxically represent a deterrent to the application of the technique and to date the employment of PTR-ToF-MS was seldom reported in the field of nosespace analysis [3].

In the present work PTR-ToF-MS was applied to the determination of inter-individual differences through the study of the interaction between tasters and a real-life, unmodified food matrix. The investigation focused on coffee, due to its role as "golden standard" in PTR-MS based food analysis. A practical recipe for the easy handling of nosespace data, based upon a straightforward six-step procedure, was here proposed and validated on a real dataset.

Experimental Methods

Tasting protocol

Coffees prepared from three different commercial Arabica blends (strong roasting, medium roasting and decaffeinated) were assessed by five panelists (three females and two males, aged between 25 and 37) in triplicate. The experiments were distributed over three separate sessions performed on three consecutive days. During each session the three types of coffee were tasted by each panelist following a randomized order of presentation. The tasting protocol was the following: breathing for 30 seconds, then swallowing of a single small aliquot (7.5 ml) of coffee, served at controlled temperature (60 °C) and finally breathing for 3 minutes.

Instrumental analysis

Measurements were carried out using a commercial PTR-TOF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria). The PTR-MS inlet (PEEK tube, 0.055" in diameter, heated at 110 °C) was connnected to the panelist's nose through an ergonomic nosepiece. Exhaled air was sampled at a flow rate of 400 sccm. Spectra were acquired at 1 cycle s^{-1} and the sampling time per channel in the TOF wass 0.1 ns, amounting to 350,000 channels for a mass spectrum ranging from m/z 10 to 400. All measurements were carried out under drift tube conditions of 550 V, drift pressure of 2.30 mbar, temperature 110 °C, and E/N value of 134 Td (Td = Townsend; 10^{-17} cm^{-2} V^{-1} s^{-1}).

Software packages

The software tools used in this study were developed using MATLAB (MathWorks, Natick, United States) and R (R Foundation for Statistical Computing, Vienna, Austria).

Results and Discussion

The overall data amounted to about 10,000 spectra, acquired over three days and 45 nosespace sessions. The demanding task of data analysis was greatly simplified by the employment of an in-house developed software package that operates in MATLAB environment and allows for the easy handling of PTR-ToF-MS spectra [4]. The resulting calibrated and extracted data consisted of a single spreadsheet of roughly six million cells (617 mass peaks x 9,493 spectra). A six-step procedure is here proposed for the analysis and interpretation of the data:

(a) Preliminary filtering: all mass peaks whose cumulative profiles were lower than 1 ppb in maximum value were discarded.

(b) Peak-like feature recognition: within each profile the 30s before and after sample introduction were compared by means of a one-tailed Student's t-test. All profiles where a significant increase was observed after sample introduction were further employed. A core subset of 142 mass peaks was thus obtained. Most of these could be tentatively assigned to well-known coffee volatiles.

(c) Profile baseline subtraction: the first 30s of acquisition (*i.e.* the panelist's breath) were subtracted from each profile; this evened out inter-individual differences that were not linked to the interaction with the food sample.

(d) Parameter extraction: from each profile six parameters were obtained, some related to the amounts of volatiles released (maximum, mean and area under the curve), others to the shape of the peak (median, slope, time to reach the maximum).

(e) Generation of a "custom release chart" for each panelist: the aim was to portray, within a single screenshot, the complexity of the results. By way of example, the comparison between the

peak maxima given by two panelists on two coffees is represented in figure 1. It was possible to evaluate graphically that, not only the two assessors significantly differed in most of the reported mass peaks, but more importantly they responded in different ways to different samples. In fact, while many volatiles displayed higher release maxima with strong roasting coffee for panelist 1, the opposite result was obtained with panelist 2.
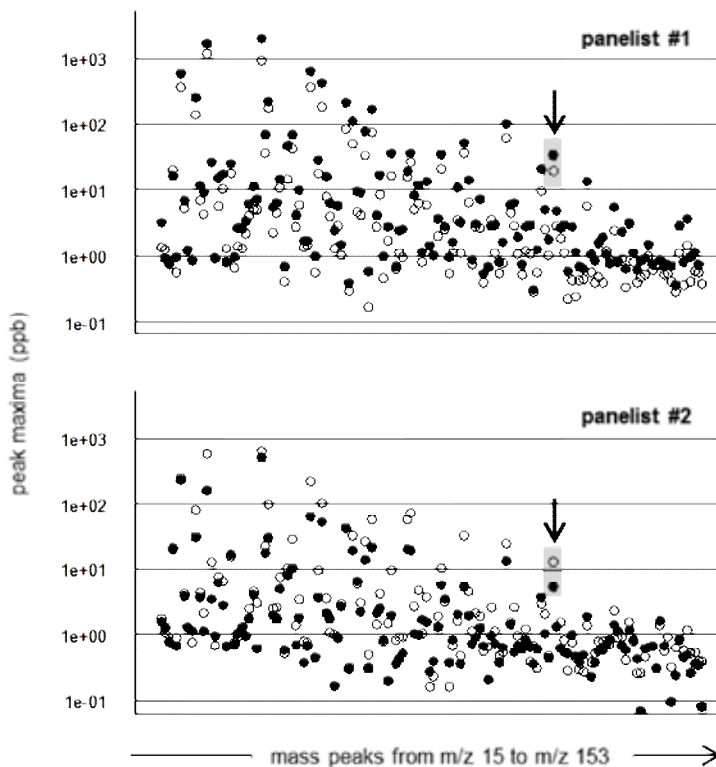
Figure 1: Comparison of nosespace custom release charts obtained on two panelists and two types of coffee (● strong roasting, ○ medium roasting).Each circle indicates the maximum of the release profile for a given mass peak. One hundred and forty-two peaks are represented, with masses ranging from m/z 15 to m/z 153.The highlighted section corresponds to mass peak m/z 111.0445, tentatively assigned to methyl-furfural.

(f) Comparison of selected nosespace profiles: it was possible to ascertain that, in spite of day-to-day variability that characterized all individual responses, volatile release profiles (and the corresponding peak parameters) were reproducible enough to establish statistically significant differences between samples and/or panelists. This is shown in more detail for one of the mass peaks in figure 2 (m/z=111.0445, tentatively assigned to methyl-furfural).

The results demonstrate the potentialities of PTR-ToF-MS nosespace in the analysis of food-consumer interaction. In the assessment of three samples of coffee by five panelists reproducible

differences in the volatile release profiles could be measured. The question is whether these instrumentally measured differences have a practical impact in terms of individual sensitivity and preference.
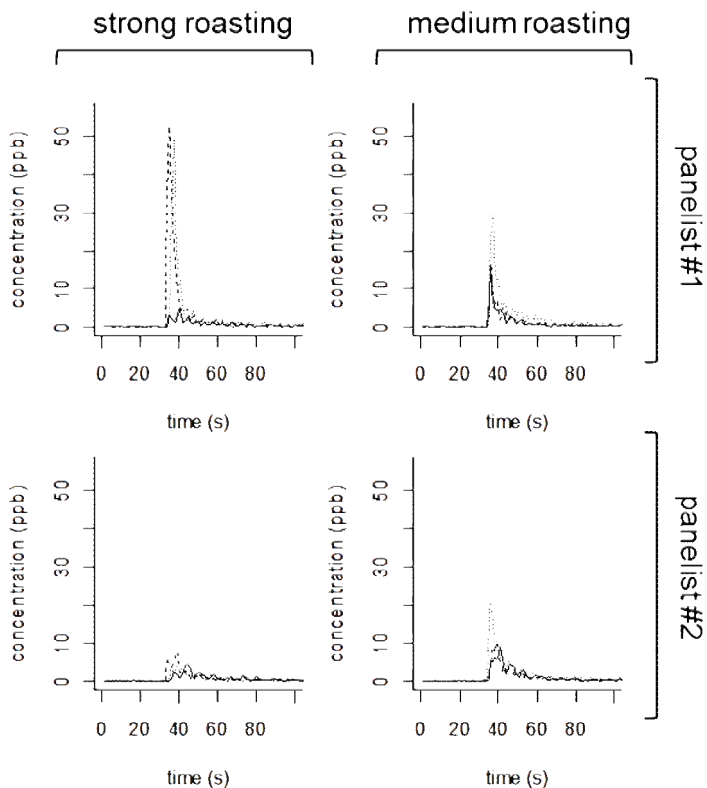
Figure 2: Release profiles obtained on two panelists and two types of coffee for mass peak m/z 111.0445, tentatively assigned to methyl-furfural (three replicates for each condition).

References

[1] I. Menashe, O. Man, D. Lancet, and Y. Gilad, Different noses for different people, Nature Genetics, 34, 143-144, (2003).

[2] F. Biasioli, C. Yeretzian, F. Gasperi, and T. Märk, PTR-MS monitoring of VOCs and BVOCs in food science and technology, Trends in Analytical Chemistry 30, 968-977, (2011).

[3] S. Heenan, C. Soukoulis, P. Silcock, A. Fabris, E. Aprea, L. Cappellin, T.D. Märk, F. Gasperi, and F. Biasioli. PTR-ToF-MS monitoring of in-vitro and in-vivo flavor release in cereal bars with varying sugar composition, Food Chemistry 131, 477-484, (2011).

[4] L. Cappellin, F. Biasioli, P. Granitto, E. Schuffried, C. Soukoulis, F. Costa, T. Märk, and F. Gasperi, On data analysis in PTR-ToF-MS: from raw spectra to data mining, Sensors and Actuators B 155, 183-190 (2011).

Rapid Characterization of Dry-Cured Ham Volatile Compound Profile by PTR-Tof-MS: Effect of Geographical Origin, Rearing System and Cross-Breeding

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Abstract

Dry-cured ham is a valuable traditional foodstuff highly appreciated by consumers due to its unique flavour characteristics that depend on ripening conditions [1] and raw meat characteristics, i.e. animal age and genotype and type of feed during the fattening period [2, 3].

In this study we consider the effect of three different factors which can affect the final volatile profile of dry-cured hams: the geographical origin, and so the characteristics of the protected designation of origin (PDOs); the rearing system of the pigs, and the cross-breeding.

The effect of the geographical origin was researched using dry-cured hams from 4 PDOs: Italian PDOs *Prosciutto di Parma* (26 hams), *Porsciutto di San Daniele* (25 hams) and *Prosciutto Toscano* (29 hams), and the Spanish Iberian dry-cured ham PDO *Dehesa de Extremadura* (20 hams). The effect of the rearing system of the pigs on the final volatile profile of the dry-cured hams was investigated using the 20 Iberian dry-cured hams from the *Dehesa de Extremadura* PDO, 10 from pigs fattened outdoors on concentrated feed (*Campo*) and 10 from pigs fattened outdoors on acorn and pasture (*Montanera*) [4]. At last, the effect of the cross-breeding of the pigs was studied using the dry-cured hams from the Italian PDOs, which were produced from two different industrial cross-breeding pigs, a reference industrial hybrid (Italian Large White x Italian Landrace) and a Goland hybrid from the Italian Breeders Association. The hams were obtained and processed as fully described in Sánchez del Pulgar et al [5, 6]. From each ham a piece of the *Biceps femoris* muscle was taken, and 3 meat cubes of 1cm^3 (3 replicates) were prepared. The cubes were introduced into 40ml vials and equilibrated at 37°C for 30 min in a water bath prior to analysis.

Measurements were carried out using a commercial PTR-ToF-MS 8000 apparatus by direct injection of the head space mixture into the PTR-ToF-MS drift tube via a heated (110°C) peek inlet for 30s, taking 30 average spectra. Internal calibration of ToF spectra was performed off-line [7]. Peak detection and area extraction were performed according to the procedure described in Cappellin et al [8]. Principal components analysis (PCA) and Penalized

Discriminant Analysis (PDA) [9] were performed. To evaluate the results of the classification method we used a leave-group-out (LGO) method.

The rapid analysis of the headspace of the dry-cured hams by PTR-ToF-MS resulted in more than 600 mass peaks, and these data were used to perform the above mentioned analysis. Both the PCA and the PDA allowed a good separation of the dry-cured ham samples from different PDOs [5], probably due to the differences in the PDOs requirements, such as pig's breed (hybrid pigs from various crossing breeds such as Large Withe, Landrace and Duroc-Jersey in Italian PDOs, only Iberian pigs or their direct crossbreeds with Duroc-Jersey for Spanish Iberian hams [10]), salting process (use of small amounts of nitrates and nitrites allowed or banned) and ripening duration (12 months for Italian PDOs and at least 18 months for Iberian dry-cured ham PDOs). The statistical analyses allowed also the separation of the dry-cured Iberian ham samples from pigs fattened on different diets [6]. Nevertheless, it was not possible the discrimination of the dry-cured hams of the Italian PDOs according to the cross-breeding of the pigs, which indicates that this factor has a little effect on the final volatile profile of the dry-cured ham, much lower than other factors as the fattening diet of the pigs and the ripening conditions of the hams [2, 10].

Therefore, the geographical origin or the PDO (and so the ripening conditions and its duration) has a stronger effect on the final volatile profile of dry-cured hams than the fattening diet of the pigs, while the effect of the industrial cross-breeding seems to be negligible.

References

[1] J. Ruiz, J. Ventanas, R. Cava, A. Andrés and C. García. Volatile compounds of dry-cured Iberian ham as affected by the length of the curing process. Meat Science, 52, 19-27 (1999).

[2] A.I. Carrapiso, F. Bonilla and C. García. Effect of crossbreeding and rearing system on sensory characteristics of Iberian ham. Meat Science, 65, 623-629 (2003).

[3] T. Pérez-Palacios, T. Antequera, M.L. Durán, A. Caro, P.G. Rodríguez and J. Ruiz. MRI-based analysis, lipid composition and sensory traits for studying Iberian dry-cured hams from pigs fed with different diets. Food Research International, 43, 248-254 (2010).

[4] Real Decreto 1469/2007, de 2 de noviembre, por el que se aprueba la norma de calidad para la carne, el jamón, la paleta y la caña de lomo ibéricos. B.O.E. n. 264, November 3rd 2007, 45087-45104.

[5] J. Sánchez del Pulgar, C. Soukoulis, F. Biasioli, L. Cappellin, C. García, F. Gasperi, P. Granitto, T.D. Märk, E.; Piasentier and E. Schuhfried. Rapid characterization of dry cured ham produced following different PDOs by proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS). Talanta, 85, 386-383 (2011).

[6] J. Sánchez del Pulgar, C. Soukoulis, A.I. Carrapiso, , L. Cappellin, P. Granitto, E. Aprea, A. Romano, F. Gasperi and F. Biasioli. Effect of the pig rearing system on the final volatile profile of Iberian dry-cured ham as detected by PTR-ToF-MS.

[7] L. Cappellin, F. Biasioli, A. Fabris, E. Schuhfried, C. Soukoulis and T.D. Märk. Improved mass accuracy in PTR-TOF-MS: Another step towards better compound identification in PTR-MS. International Journal of Mass Spectrometry, 209, 60-63. (2010).

[8] L. Cappellin, F. Biasioli, P. Granitto, E. Schuhfried, C. Soukoulis, F. Costa and T.D. Märk. On data analysis in PTR-TOF-MS: From raw spectra to data mining. Sensors and Actuators B-Chemical 155, 183-190 (2011).

[9] P. Granitto, F. Biasioli, E. Aprea, D. Mott, C. Furlanello, T.; Märk and F. Gasperi. Rapid and non-destructive identification of strawberry cultivars by direct PTR-MS headspace analysis and data mining techniques. Sensors and Actuators B-Chemical, 121, 379-385 (2007).

[10] A.I. Carrapiso, A. Jurado and C. García. Effect of crossbreeding and rearing system on Iberian ham volatile compounds. Food Science and Technology International, 9, 421-426 (2003).

Recent Applications of PTR-ToF-MS in Coffee Research

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Abstract

The flexibility, speed and analytical quality of PTR-MS transformed this technique from its early days of basic research applications to a highly sought-for analytical technology in applied research. This includes fields as diverse as environmental research, waste incineration, food and flavor science, homeland security, biological research, process monitoring, indoor air quality, medicine, biotechnology and more. It can be used either as a stand-alone technology or be integrated into a broader multi-method analytical platform. Among the various applied fields where PTR-MS is having a significant and lasting impact, research on coffee has exceptionally profited from PTR-MS as well as contributed to its progress, expansion and visibility. Here we would like to demonstrate, on a series of concrete examples, the role that PTR-MS is playing in the research on coffee.

Introduction

While coffee is one of the most consumed beverages in modern societies, it is also a highly complex research subject. Furthermore, it is a product of huge economic importance to coffee growing and coffee consuming countries. Coffee is the second most valuable commodity exported by developing countries, after crude oil. Total direct employment in the coffee sector amount to approximately 26 million and around 110 million people make their living from coffee. In 2010, with an annual production of 133 million bags (60 kg/bag) the value of the traded coffee amounted to about 35 billion $ and was the second most performing commodities, with 45% ROI (next to cotton).

The application of PTR-MS in coffee research started around 1996 when Prof. Werner Lindinger and Dr. Yeretzian met for the first time in 1996 at the SASP96 conference of Engelberg / Switzerland. In the meantime PTR-MS has become an established technology that has made various significant contributions to the progress of this field *(1-7)*. Indeed PTR-MS is used in projects along the whole value of coffee, as demonstrated in Figure 1.

Here we would like to give an overview of some selected, recent applications of PTR-MS on applied coffee projects.

Figure 1: *PTR-MS is used in research all along the value chain of coffee.*

On-line Analysis of the Coffee Roasting for Selected Coffee Origins

As a first application, we will discuss the analysis of coffee of different origins, namely *coffea arabica* from Colombia, Guatemala, and Ethiopia and *coffea canephora var. robusta* from Indonesia along different time-temperature roasting profiles, as show in Figure 2.
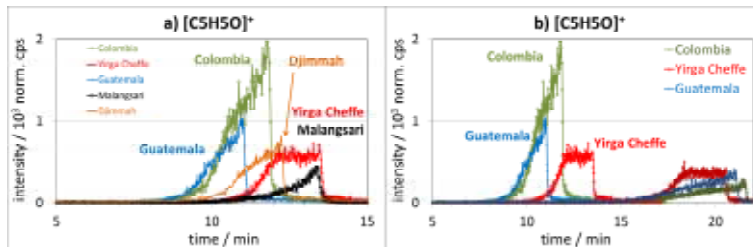
Figure 2: Time-intensity profiles of one VOC ($[C5H5O]^+$) during the time-temperature roasting profile of a) about 12 min and b) about 12 min and 20 min for the different coffees Colombia, Yirga Cheffe, Djimmah (only 12 min), Guatemala and Malangsari (only 13 min).

Air-Water Partition Coefficients

A second application concerns the measurement of water-air partition coefficients (Henry-Law-Constants) over an extended temperature range, using the experimental setup shown in Figure 3. These will be discussed based on a few selected volatile organic compounds.
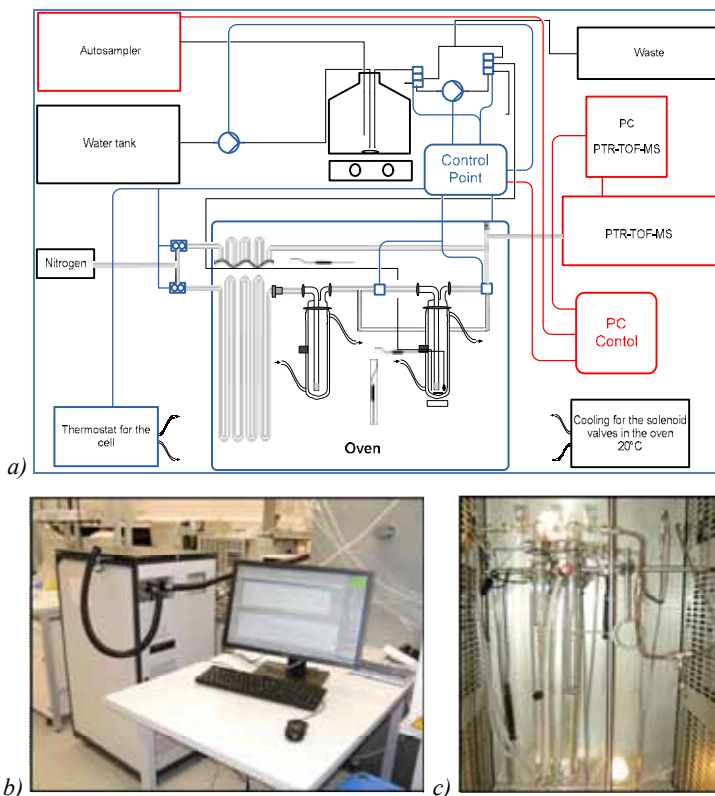
Figure 3: Experimental setup for measuring the air-water partitioning coefficients of volatile organic compounds. a) Schematic drawing of the automated measuring setup. b) PTR-ToF-MS. c) stripping cells insight the oven.

Correlation of PTR-MS Spectra with Sensory Profiles

Finally, an analytical tool to predict the flavor profile of coffee was developed based on measurements of the headspace of coffee with proton transfer reaction time of flight mass spectrometry and solid phase micro extraction gas chromatography coupled to mass spectrometry and correlating the instrumental data to sensory profiles by an expert panel as schematically presented in Figure 4.
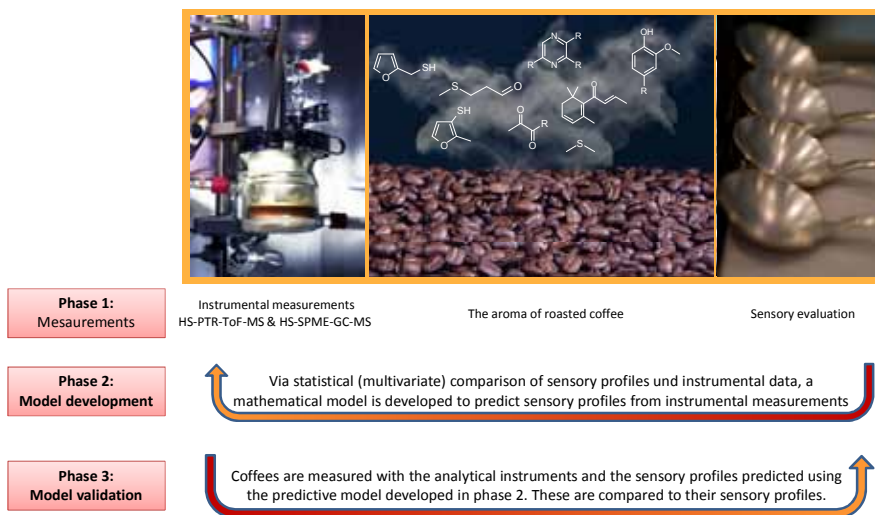
Figure 4: Schematic representation of the three phases in developing the predictive model.

References

[1] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Maerk, H. Seehauser, R. Schottkowsky, P. Sulzer, T. D. Maerk, A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) Int.J.Mass Spec. 286, 122-128, (2009).

[2] A. N. Gloess, B. Schönbächler, A. Vietri, S. Bongers, T. Koziorowski, C. Yeretzian, Effect of roasting on the aroma of coffee. Online analysis of roasting using proton transfer reaction mass spectrometry GIT Labor-Fachzeitschrift 55, 712-715, (2011).

[3] F. Wieland, A. Gloess, M. Keller, A. Wetzel, S. Schenker, C. Yeretzian, Online monitoring of coffee roasting by proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS): towards a real-time process control for a consistent roast profile Anal.Bioanal.Chem. 402, 2531-2543, (2011).

[4] C. Yeretzian, A. Jordan, H. Brevard, W. Lindinger, On-line Monitoring of Coffee Roasting by Proton-Transfer-Reaction Mass-Spectrometry On-line Monitoring of Coffee Roasting by Proton-Transfer-Reaction Mass-Spectrometry, pp. 112-123 .

[5] C. Yeretzian, A. Jordan, R. Badoud, W. Lindinger, From the green bean to the cup of coffee: investigating coffee roasting by on-line monitoring of volatiles Eur.Food Res.Technol. 214, 92-104, (2002).

[6] R. Dorfner, T. Ferge, A. Kettrup, R. Zimmermann, C. Yeretzian, Real-time monitoring of 4-vinylguaiacol, guaiacol and phenol during coffee roasting by resonant laser ionisation time-of-flight mass-spectrometry J.Agric.Food Chem. 51 , 5768-5773, (2003).

[7] R. Dorfner, T. Ferge, C. Yeretzian, A. Kettrup, R. Zimmermann, Laser mass spectrometry as on-line sensor for industrial process analysis: Process control of coffee roasting Anal.Chem. 76, 1386-1402, (2004).

Applications of PTR-TOF-MS in food chemistry: discrimination of isobaric aroma compounds and monitoring of lipoxygenase-derived volatile formation

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Abstract

Detailed knowledge on flavour release from food matrices can help to greatly improve a food's flavour profile, which is of high interest to the food industry due to consumer demand. Several milestone studies have been carried out by traditional PTR-MS [1]; however, monitoring the flavour release of nominally isobaric aroma compounds from model or complex food matrices is hindered by the known limitations of the quadrupole mass filters.

To initially assess PTR-TOF-MS performances and detection limits for food-flavour applications we investigated the releases of four pairs of nominally isobaric aroma compounds in the dynamic headspace of aqueous solutions. Compounds were matched to achieve nominally isobaric pairings of their molecular ions and/or main fragment, as follow: cis-3-hexenol and 2,3-pentanedione (nominal m/z 101), benzaldehyde and m-xylene (m/z 107), ethyl butanoate and 2-methylbutanol (m/z 89), butyl isovalerate and 1-hexanol (m/z 103). By using a commercial data visualisation and processing software it was possible to separately fit and integrate the partly overlapping peaks with a centre of mass separation down to at least 0.036 Da (Δm_{FWHM}), thus proving the instrument discrimination power and revealing the underling aroma release profile. An example is shown in Fig.1 for the pair cis-3-hexenol and 2,3-pentanedione. The observed differences in signal intensities, mainly attributable to the compounds' different physicochemical properties, would not be discernible by monitoring the release with conventional PTR-MS.

The viability of performing dynamic headspace measurements of more complex food systems with PTR-TOF-MS was tested by monitoring the enzyme-catalysed volatile formation from the interaction of lupin lipoxygenase (LOX) with linolenic acid substrate at two different pH (6.9 and 9) and three temperatures (25, 33 and 43°C). In Tab. 1 we provide the first report of on-line monitoring of the dynamic release of a wide range of volatile compounds from this enzymatic reaction [3]. The attributed chemical identification is based on exact formula weight and matching with the sparse literature reports [4].
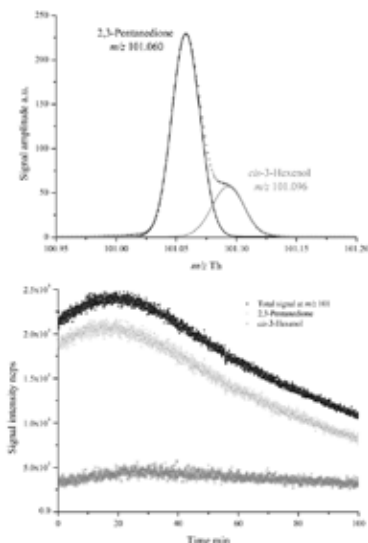
Figure 1 Top: PTR-TOF-MS spectra at nominal m/z 101, displaying the molecular ions of 2,3-pentanedione and cis-3-hexenol. Gaussian peak functions have been fitted to the data in arbitrary units (a.u.). Bottom: release from water at 37°C of the compound pair at initial aqueous concentration of 4.43 µg ml-1. The signals of exact masses of each compound (grey) are plotted with the total nominal m/z signal (black).

m/z	pH 6.9			pH9			Tentative identification
	25°C	33°C	43°C	25°C	33°C	43°C	
45.036	105	104	291		—		Acetaldehyde
57.040	447	548	1335	499	716	1249	
59.041	94	109	548	81	99	181	Acetone
63.037	36	36	162		—		
65.062		—		10	17	30	
69.061	110	156	410	139	143	251	Isoprene
83.079	306	435	2539	301	927	1014	
87.074	145	224	1312	164	197	584	Pentanal
99.079	27	30	116		—		
101.082	378	603	6225	404	1377	2374	Hexanal
105.095	32	48	362	39	46	157	
111.120	16	24	137		—		
113.096	117	163	1116	125	249	781	Heptenal
117.087	22	21	49		—		
119.107	50	87	1365	50	155	382	
127.107	64	86	520	90	303	514	Octenal
131.108	20	19	84		—		
139.115	10	12	42		—		Nonadienal
153.122	6	8	19	8	22	17	Decadienal
155.106	24	25	53	35	20	37	

Table 1: The wide range of compounds derived from LOX-catalysed reaction of linolenic acid. Signal intensities are in ncps.

References

[1] F. Biasioli, F. Gasperi, C. Yeretzian and T. D. Märk, PTR-MS monitoring of VOCs and BVOCs in food science and technology, TrAC Trends in Analytical Chemistry 30(7), 968-977 (2011).

[2] E. Zardin, O. Tyapkova, A. Buettner and J. Beauchamp, Performance assessment of proton-transfer-reaction time-of-flight mass spectrometry (PTRTOF-MS) for analysis of isobaric compounds in food-flavour applications, LWT – Food Science and Technology, submitted September 2012.

[3] E. Zardin, S. Bader, Proton-Transfer-Reaction time-of-flight mass spectrometry (PTR-TOF-MS) as a tool for monitoring lipoxygenase-derived flavour compounds, in prep.

[4] F. Ullrich, W. Grosch, Identification of the most intense volatile flavour compounds formed during autoxidation of linoleic acid, Zeitschrift für Lebensmitteluntersuchung und Forschung A, 184(4), 277-282 (1987).

Instruments & Technology and Future Trends

From Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) to Universal Trace Gas Analysis with Selective-Reagent-Ionization Mass Spectrometry (SRI-MS) in Kr[+] mode

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Abstract

Although PTR-MS is an outstanding and well established technology for trace gas analysis, it has one disadvantage: only compounds possessing a higher proton affinity than water or, in case O_2^+ is used as reagent ions, ionization energies below 12.1 eV can be ionized. Thus, especially in environmental research, one of the main application fields of PTR-MS, some important substances are not detectable.

Here we want to present a new type of Selective-Reagent-Ionization Mass Spectrometry (SRI-MS) instrument that can be used for the analysis of nearly all known compound classes by using both proton-transfer-reaction (PTR) and/or charge-transfer-reaction (CTR) ionization. The latter can be performed with the help of reagent ions (especially Kr^+) which possess higher ionization energies than common air constituents. Consequently now trace volatile organic compounds (benzene, toluene, etc.) as well as very important inorganic substances (CO, CO_2, NO_2, etc.) can be analyzed with just one SRI-MS instrument.

For proof-of-principle measurements we analyzed different gas standards containing molecules possessing ionization energies all the way up to 14 eV (CO). In order to demonstrate a possible field of application we additionally present measurements of different exhaust gases.

Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well established technology for real-time trace gas analysis in the fields of environmental research [1], food and flavor science [2], medicine and homeland security [3]. However there is one drawback: the PTR from H_3O^+ to the sample molecule is defined by the proton affinity (PA) of the molecule, which has to be higher than the PA of water.

Since most of the volatile organic compounds posses quite high PAs (the National Institute of Standards and Technology NIST hosts an extensive database of PAs [4]), and common air compounds like N_2, O_2, CO_2 or Ar have lower PAs than water, normally air can be used as buffer gas in PTR-MS instruments. Consequently the sampling process is very easy and the sensitivity is not reduced by any buffer gas dilution.

In order to make also charge-transfer-reactions (CTR) and other molecule reactions available for PTR-MS instruments we presented 2009 the so-called "Switchable Reagent Ions" (SRI) feature as an add-on to our instruments [5]. Since then it is possible to switch between H_3O^+ (PTR) and NO^+

or O_2^+ as reagent ions. Although the design of the ion source and the vacuum conditions had to be changed slightly for the present adaption, there is still no need to use a mass filter between the ion source and the drift tube; high reagent ion purity is achieved via the sophisticated ion source design. This unique feature of IONICON's instruments distinguishes them from similar technologies which use a signal diminishing ion-selection system (e.g. quadrupole mass filter) following the ion source.

The number of ionizable compounds could already be extended with rolling out the SRI feature in 2009, since with O_2^+ (ionization energy (IE): 12.07 eV [4]) as reagent ions it is possible to analyze via electron (charge) transfer reactions several compounds which possess lower PAs than water, like e.g. ethylene (C_2H_4, IE: 10.51 eV [4]) and acetylene (C_2H_2, IE: 11.40 eV [4]). However, there are still some very important substances (e.g. for pollution analysis, engine exhaust studies, etc.), i.e. CO, CO_2, N_2O, SO_2, etc., which until now could not be detected.

Here we want to present a new SRI-MS technology: a method combining a common PTR-MS instrument with chemical ionization by Kr^+ or Xe^+ resulting in a universal trace gas analyzer capable of PTR and CTR ionization (patent pending PCT/EP2011/064170). We call this new feature: "SRI+" [6]. Furthermore we want to show results of a possible field of application.

Experimental Methods

Detailed descriptions of the well-known technology of the PTR-MS instrument can be found elsewhere in literature [e.g. 7,8]. For this present innovation the principal setup of the utilized PTR-TOF 8000 stays the same.

The biggest challenge of the present innovation was to find a way to overcome the limitation working with PTR-MS that the reagent ion has to have an IE lower than the common components of air (e.g. O_2). This is of great importance because if the reagent ion has an IE higher than 12 eV it would immediately react with O_2 (approx. 20% in air) so that there are hardly any ions left to react with trace gas compounds. Therefore we dilute the sample air with helium as carrier gas since helium has the highest known IE of 24.59 eV [4]. As reagent ion we choose krypton (Kr; IE:14.00 eV [4]) for the present measurements. Additionally it is also possible to use xenon (Xe, IE:12.13eV [4]) in this modified setup. Xe can be an important alternative for applications where oxygen cylinders are not allowed, e.g. because of fire protection or ex-proof regulations.

As mentioned before, even in this modified version no mass filter is needed between the ion source, which generates the reagent ions, and the drift tube, where the ionization of the trace compounds takes place. Kr and Xe are provided from external gas cylinders and introduced directly into the ion source. In the hollow discharge ion source the reagent ions are produced at very high purity levels solely by the source design, the vacuum conditions and the electric fields in the ion source and the drift tube.

Results

Impurities originating from the ion source operated in Kr^+ mode were determined using pure He as a buffer gas. At an outstandingly high ion yield of about 9×10^6 cps (counts per second) for Kr^+ the two major impurities can be identified as KrH^+ and He^+ with 4.3% and 1.8%, respectively; whereas other ions, such as e.g. O_2^+, Kr^{++}, NO^+, etc., contribute with less than 0.5% in total. These results underline the above-mentioned statement that despite of the fact, that no mass filter is used to select the reagent ions in this modified PTR-MS instrument, the reagent ion purity is exceptionally high (considering that the ion source was primarily built for an efficient and pure production of H_3O^+). Following these impurity determinations, we gradually analyzed a series of

certified gas standards containing the molecules CH_4, CO, CO_2, N_2O, NO_2, H_2S, SO_2 and SO_2F_2. Please note that most of these compounds cannot be analyzed with PTR-MS even if it is equipped with SRI, i.e. no matter if H_3O^+, O_2^+ or NO^+ is used as reagent ions. However, with Kr^+ we could detect all of these compounds unambiguously, even though this list includes isobars (CO^+ and N_2^+ (impurity), CO_2^+ and N_2O^+, $^{18}OO^+$ (impurity) and H_2S^+, respectively, possess the same nominal masses). These standard gas studies can therefore be considered as a proof-of-principle that the introduction of Kr^+ as reagent ions indeed transforms a PTR-MS instrument to a universal trace gas analyzer.

Finally we want to present the instrumental performance of an SRI+ equipped IONICON PTR-MS instrument by means of real-life examples from typical fields of application. In figure 1 a section of a mass spectrum obtained with a PTR-TOF 8000 with SRI+ (Kr^+ mode) is shown. Prior to the analysis engine exhaust gas from a car was collected in a PTFE bag and transported to the laboratory. Amongst an ample number of well known exhaust compounds which we could detect in the sample figure 1 focuses on the mass range around carbon monoxide, an inorganic molecule that could never be analyzed with PTR-MS before. Although CO^+ and the impurity N_2^+ differ by only 0.01 amu in their exact mass, they can clearly be separated and identified due to the high mass resolution of the PTR-TOF 8000utilized for this study.
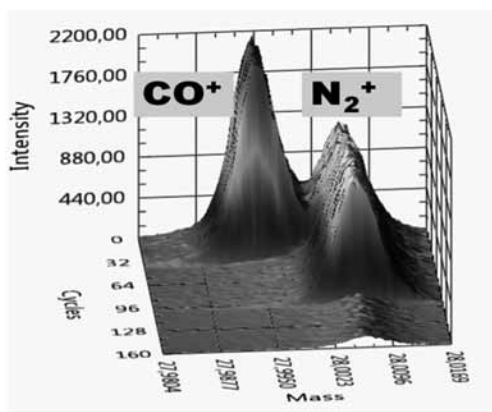
Figure 1: Section of a mass spectrum obtained from engine exhaust emission. Because of the high mass resolution CO^+ and N_2^+ can be clearly separated.

Discussion

In summary, with IONICON's SRI-MS instrument it is now possible to switch between H_3O^+, O_2^+, NO^+, Kr^+ and Xe^+; thus there are virtually no limitations on substance classes and subsequently on fields of application anymore. All advantages of common PTR-MS (H_3O^+ mode) are preserved, while the possibility of utilizing Kr^+ (and Xe^+, which is not discussed here) as an additional ionizing agent is added. With SRI-MS it is possible to analyze a largely increased number of substance classes (including typical exhaust or fumigation gases like CO and SO_2F_2, respectively) thereby taking PTR-MS a huge step forward towards a universal gas analyzer with the advantages of the exceptional sensitivity as well as low online detection limits, PTR-MS is

known for and the versatility of classic direct injection mass spectrometry technologies. Because of the sophisticated ion source design and the fact that no mass filter between the ion source and the reaction region is installed, the reagent ion yield reaches a remarkably high value of 9 x 106 cps (detected after the TOF mass spectrometer, i.e. transmission dependent losses are already deducted). Moreover we have shown with various examples that the residual impurities can be separated from isobaric sample compounds with the high mass resolution of the TOF analyzer used in IONICON's PTR-TOF 8000.

Acknowledgement

References

[1] J. de Gouw, C. Warneke, T. Karl, G. Eerdekens, C. van der Veen, R. Fall, Measurement of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction, Mass Spectrometry Mass Spectrometry Reviews 26, 223–257, (2007).

[2] F. Biasioli, C. Yeretzian, F. Gasperi, T.D. Märk, PTR-MS monitoring of VOCs and BVOCs in food science and technology, Trends in Analytical Chemistry 30 (7), 968–977, (2011).

[3] P. Sulzer, F. Petersson, B. Agarwal, K.H. Becker, S. Jürschik, T.D. Märk, D. Perry, P. Watts, C.A. Mayhew, Proton transfer reaction mass spectrometry and the unambiguous real-time detection of 2,4,6 trinitrotoluene, Analytical Chemistry 84, 4161–4166, (2012).

[4] http://webbook.nist.gov/chemistry/ (6.11.2012).

[5] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, J. Herbig, L. Märk, R. Schottkowsky, H. Seehauser, P. Sulzer, T.D. Märk, An online ultra-high sensitivity proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR+SRI-MS),International Journal of Mass Spectrometry 286, 32–38, (2009).

[6] P. Sulzer, A. Edtbauer, E. Hartungen, S. Jürschik, A. Jordan, G. Hanel, S. Feil, S. Jaksch, L. Märk, T. D. Märk: From conventional Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) to universal trace gas analysis, International Journal of Mass Spectrometry 321-322,66-72, (2012).

[7] W. Lindinger, A. Hansel, A. Jordan, On-line monitoring of volatile organic compound at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS): Medical applications, food control, and environmental research, International Journal of Mass Spectrometry 173,191–24, (1998).

[8] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer, T.D. Märk, high resolution and high sensitivity time-of-flight proton-transfer-reaction mass spectrometer (PTR-TOF-MS), International Journal of Mass Spectrometry 286,122–128, (2009).

Ultra-high sensitivity Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOFMS)

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Abstract

The first commercial PTR-TOFMS instrument manufactured by IONICON Analytik was a milestone at the time of its introduction because of its sensitivity of 25 cps/ppbv and a detection limit of about 10 pptv as well as a mass resolution of over 6000 m/Δm. However, since then we continuously improved nearly every single component part, from the ion source to the vacuum system. Here we present current benchmark tests that prove an increase in sensitivity of a factor of 20, i.e. the high resolution PTR-TOF 8000 now reaches a sensitivity of up to 500 cps/ppbv and an improvement of a factor of 50 in the detection limit, which is now at about 200 ppqv. We achieve these increases in performance without any deduction in mass resolution. Furthermore, in this presentation we give an outlook on upcoming instrumental developments. First tests with PTR-TOFMS instruments equipped with these additional improvements already indicated another gain in sensitivity exceeding the original instruments by nearly two orders of magnitude.

Introduction

Although combining a Proton-Transfer-Reaction (PTR) ion source with a Time-of-Flight (TOF) mass spectrometer for the first time by different research groups was an important scientific step, the performance data were about two orders of magnitude below those from off-the-shelf PTR-QMS instruments. The main challenge is that in a TOF mass spectrometer the ions are pulsed, i.e. the instrument's sensitivity is therefore somewhat lower compared to a QMS working in continuous mode. Blake et al. and Ennis et al. [1,2] published first data of their PTR-TOF-MS prototypes showing 0.17 and 3.7 cps/ppbv sensitivity, respectively. Additionally, Blake mentioned a resolution of about 1000 m/Δm, whereas Ennis presented a detection limit of 1 ppbv. In 2009 we introduced our PTR-TOFMS system and published results [3] demonstrating that the performance data of our PTR-TOFMS (resolution over 6000 m/Δm, sensitivity of 15-25 cps/ppbv and a detection limit of about 10 pptv) were representing a milestone in the development of PTR-TOFMS technology. The importance of time-of-flight mass spectrometry has increased ever since in many different fields of application (e.g. environmental and food and flavor science [4,5]) because of high mass resolution, virtually unlimited mass range, possibility of obtaining whole mass spectra in split seconds, increasing sensitivity with increasing m/z values, etc. Very recently the PTR-TOFMS's applications even expanded into new areas like homeland security and the detection of prescribed drugs and chemical warfare agents [6]. Because of the growing importance of this technology we intended to improve sensitivity as well as the detection limits of IONICON's TOF based instruments. Here we present our latest performance data obtained with an improved PTR-TOF 8000 model.

Experimental Methods

PTR-MS, i.e. ionization via proton transfer from H_3O^+ is a well-known technology and well documented in literature. However, in the latest generation of IONICON's technology, which we call "Selective-Reagent-Ionization Mass Spectrometry" (SRI-MS), H_3O^+, O_2^+, NO^+, Xe^+ and Kr^+ can be utilized as reagent ions [7]. Due to the sophisticated design of the ion source, even in SRI-MS instruments there is no need for a mass filter between the source and the adjacent drift tube since the purity of the reagent ions is outstandingly high. Following the drift tube, where chemical ionization takes place, a transfer lens system guides the ions into the TOF mass spectrometer equipped with a microchannel plate (MCP) detector.

The PTR-TOF 8000 utilized for the present investigations was improved by adapting various kinds of parameters like e.g. the ion source, the vacuum system, etc.

Results

In order to determine the sensitivity of the improved PTR-TOFMS instrument we analyzed a certified gas standard (Restek; USA) containing compounds with molecular masses ranging from about 80 to 180 amu. The results of the sensitivity determination are shown in figure 1. At 79 m/z (protonated benzene) we achieve a sensitivity of 264 cps/ppbv, which is already more than one order of magnitude higher than the best sensitivity values we could get for the first PTR-TOFMS generation. However, with increasing masses also the sensitivity increases and reaches 479 cps/ppbv for the highest mass compound present in the gas standard (181 m/z, protonated trichlorobenzene). Further instrumental modifications are being tested at the moment and indicate another gain in sensitivity leading to more than 1000 cps/ppbv, thus representing a total increase in sensitivity of nearly two orders of magnitude compared to the original PTR-TOFMS prototype.
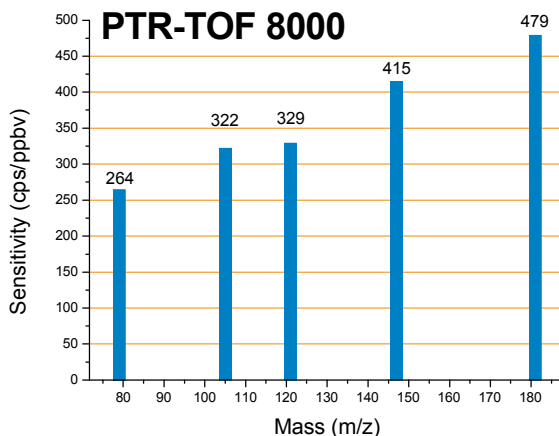
Figure 1: Measured sensitivities of the new ultra-high sensitivity PTR-TOF 8000

Limits of detection (LODs) were experimentally determined using different dilution steps of the above-mentioned gas standard. In figure 2 the results of this measurement are displayed. In order to cover a wide range of concentrations, we analyzed the resulting ion yields for several isotopes of trichlorobenzene (184.93 m/z (30.6%), 186.92 m/z (3.3%), 187.93 m/z (0.2%)) at different

dilution steps. The left side of the figure shows a concentration range from 500 pptv down to 200 ppqv in a double logarithmic diagram. The right side represents a linear close-up of the low concentration region. From these investigations we learn that the signal response of the improved PTR-TOF 8000 instrument is linear over several orders of magnitude down to a detection limit of about 200 ppqv. We want to prove with these data that for the first time we reach and even beat the detection limit of a high sensitivity PTR-QMS (ppqv region) [8] with a PTR-TOF 8000, with the advantages of high mass resolution (up to 8000 m/Δm) and increasing sensitivity for high mass compounds.
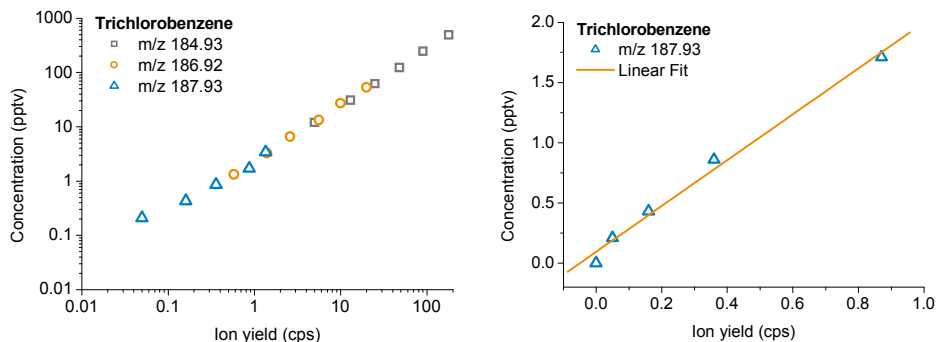
Figure 2: Linearity of the instrumental response (PTR-TOF 8000) for different compound concentrations (isotopes of trichlorobenzene at different dilution steps). Left: Log graph of a concentration range between 500 pptv and 200 ppqv. Right: Linear graph of the low concentration range down to 200 ppqv.

Discussion

Ongoing developments in PTR-TOFMS technology are bringing the instruments to new levels of sensitivity and LODs. For the very first time the performance of a high resolution PTR-TOF 8000 is comparable and, in case of LODs, even superior to that of a high sensitivity PTR-QMS 500, namely nearly 500 cps/ppbv and a LOD of about 200 ppqv (for high mass compounds around 180 amu). These outstanding instrumental performances in combination with the well-known advantages of a TOF mass spectrometer (virtually unlimited mass range, obtaining whole mass spectra in split seconds, increasing sensitivity with increasing m/z values, etc.) consolidate IONICON's PTR-MS and SRI-MS systems as the gold standard in real-time, high sensitivity, high selectivity trace gas analysis.

However, we do not stop at this point and already performed some proof-of-principle investigations on further instrumental advances. We are very confident that we will soon be able to present a PTR-TOF 8000 exceeding even these outstanding performance values, thus surpassing first generation models by nearly two orders of magnitude in terms of sensitivity, i.e. over 1000 cps/ppbv.

Acknowledgement

References

[1] R. S. Blake, C. Whyte, C. O. Hughes, A. M. Ellis, and P. S. Monks, Demonstration of Proton-Transfer Reaction Time-of-Flight Mass Spectrometry for Real-Time Analysis of Trace Volatile Organic Compounds, Anal. Chem. 76, 3841-3845, (2004).

[2] C.J. Ennis, J.C. Reynolds, B.J. Keely and L.J. Carpenter, A hollow cathode proton transfer reaction time of flight mass spectrometer, International Journal of Mass Spectrometry 247, 72–80, (2005).

[3] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer and T.D. Märk, A high resolution and high sensitivity time-of-flight proton-transfer-reaction mass spectrometer (PTR-TOF-MS), International Journal of Mass Spectrometry, 286, 122–128, (2009).

[4] F. Biasioli, C. Yeretzian, T. D. Märk, J. Dewulf and H. Van Langenhove, Direct-injection mass spectrometry adds the time dimension to (B)VOC analysis, Trends in Analytical Chemistry 30 (7),1003-1117 (2011).

[5] F. Biasioli, C. Yeretzian, F. Gasperi and T. D. Märk, PTR-MS monitoring of VOCs and BVOCs in food science and technology, Trends in Analytical Chemistry 30 (7), 968-977, (2011).

[6] T. Kassebacher, P. Sulzer, S. Jürschik, E. Hartungen, A. Jordan, A. Edtbauer, S. Feil, G. Hanel, S. Jaksch, L. Märk, C. A. Mayhew and T. D. Märk, Investigations of chemical warfare agents and toxic industrial compounds with proton-transfer-reaction mass spectrometry for a real-time threat monitoring scenario, Rapid Commun. Mass Spectrom. 27, 1–8, (2013).

[7] P. Sulzer, A. Edtbauer, E. Hartungen, S. Jürschik, A. Jordan, G. Hanel, S. Feil, S. Jaksch, L. Märk, T. D. Märk: From conventional Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) to universal trace gas analysis, International Journal of Mass Spectrometry 321–322, 66–70, (2012).

[8] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, J. Herbig, L. Märk, R. Schottkowsky, H. Seehauser, P. Sulzer, T.D. Märk: An online ultra-high sensitivity proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR+SRI-MS), International Journal of Mass Spectrometry 286, 32-38, (2009).

BVOC measurements based on NO+ ionization

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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 PTR-MS has been particularly useful in combination with micrometeorological measurement strategies. Here we investigate the use of selective reagent ion mass spectrometry (SRI-MS) based on NO^+ ionization in a conventional PTR-TOF-MS instrument. In particular we explore the possibility for atmospherically relevant applications and investigate ways to selectively distinguish important VOC species that cannot be easily separated using conventional PTR-MS.

Introduction

Volatile organic compounds (VOCs) critically influence the composition of the Earth's atmosphere by fueling tropospheric chemistry [1], thereby modulating its oxidation capacity and providing condensable material for organic aerosol formation [2]. Biogenic VOC emissions are often dominated by 2-methyl-1,3-butadiene (isoprene) and 2-methyl-3-buten-2-ol (232 MBO).

With the emergence of fast online measurement techniques, ecosystem fluxes of both species are increasingly obtained by the eddy covariance technique. Proton-transfer-reaction mass spectrometry (PTR-MS) ([3],[4],[5]) has so far been the technique of choice [6]. Previous studies [7] have identified the presence of a host of biogenic C5 alcohols and aldehydes, which collisionally dissociate or dehydrate and could potentially interfere with the detection of isoprene using hydronium ion chemistry in PTR-MS. In many places isoprene dominates over most other BVOCs and these interferences are often shown to be minor ([8], [9], [10]); however measurements, particularly in coniferous ecosystems, can be more challenging due to the concomitant emission of isoprene and 232 MBO. In PTR-MS 232 MBO undergoes collisional dissociation and a dehydration reaction leading to the dominant ion fragment m/z 69^+ Th (parent ion minus an H_2O group); typically about 25% remains on the parent ion (m/z 87^+ Th). Theoretically it should be possible to distinguish 232 MBO and isoprene, as long as a significant portion of both compounds enables investigating the ratio of the ions m/z 87^+ Th and m/z 69^+ Th. However this exercise becomes increasingly difficult when isoprene concentrations are comparably low (e.g. <30%) relative to 232 MBO.

Need for improved detection of these species is also corroborated by the fact that conventional GC (gas chromatographic) techniques can be prone to humidity and oxidant dependent detection uncertainties [11]. Baker et al. [12] have shown that anytime a sample treatment involves heating,

232MBO can dehydrate (e.g. GC sample treatment). Here we test the feasibility of using NO^+ ion chemistry to selectively distinguish isoprene and 232 MBO using SRI-MS technology (charge transfer reaction mass spectrometry).

Experimental Methods

The study was located at the Manitou Forest Observatory near Woodland Park, Colorado, USA (2290 m elev., lat. 39°6'0" N, long. 105°5'30" W) and took place in July 2011. The site is representative of the montane ponderosa pine zone in the Front Range which extends from southern Wyoming to northern New Mexico. 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 soils. The average tree height surrounding the measurement tower was 18.5m.

Measurements were taken from a 30 m tall tower. All instruments sampled off an approximately 35 m long Teflon line (OD: 3/8"; ID: 0.33"), pumped at a speed of about 30 l/min, so that overall delay times were measured between 3 and 5 s.

A Proton-transfer reaction time of flight mass spectrometer (PTR-TOF-MS) based on a high resolution time of flight mass spectrometer (HTOF-MS, Tofwerks, Switzerland) and developed at the University of Innsbruck [13] was operated using protonated water (H_3O^+) as reagent ion. Here we operated the instrument at 60°C, a drift tube voltage of 580V and a drift tube pressure of 2.3 mbar. These conditions resulted in an E/N ratio of about 125 Townsend (Td) (E being the electric field strength and N the gas number density; 1 Td=10^{-17} Vcm^2). Parallel measurements using NO^+ ionization were performed using a SRI-TOF-MS 8000 apparatus from Ionicon Analytik GmbH, Innsbruck (Austria) [14]. The ionization conditions in the drift tube were controlled by drift voltage (530V), drift temperature (60 °C) and drift pressure (2.3mbar) resulting in an E/N of about 115 Td. The achieved purity of the NO^+ signal was 93% in the field and 95% for laboratory calibration experiments. Knighton et al. [15] have observed high purity of NO^+ production and concluded that NO_2^+ formation can be largely suppressed by adjusting the ion source extraction voltage. Here settings of 6-8 mA ion current, an extraction voltage of 120V and a source valve setting of 35% led to a fraction of about 1% NO_2^+ relative to NO^+. O_2^+ and H_3O^+ varied between 2-4% and 1-3 % respectively relative to the NO^+ signal.

Results and Discussion

The reaction between NO^+ and 232 MBO proceeds via hydroxide ion transfer [16] and is detected on molecular ion m/z 69.0704^+ Th corresponding to ($C_5H_9^+$); isoprene exhibits a low ionization potential (IP of 8.84 eV) and therefore undergoes charge transfer leading to an observed m/z 68.0626^+ Th. Figure 1 shows mass spectra of 232 MBO and isoprene ions measured during laboratory experiments. The major product ion (> 98%) for 232 MBO is detected on molecular ion m/z 69.0704^+ Th corresponding to ($C_5H_9^+$); isoprene is observed on m/z 68.0626^+ Th.
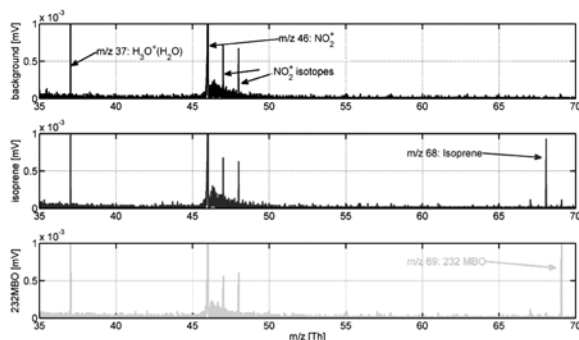
Figure 1: Plot of the mass spectrum between m/z 35+ Th and m/z 70+ Th for a blank (top panel), an isoprene standard (middle panel) and 232 MBO standard (lower panel). Ion impurities are labelled on the top panel.

A field test was performed between August 8 and 16 2011, when a PTR-TOF-MS was operated in standard H_3O^+ mode, while the a SRI-TOF-MS instrument was operated in NO^+ mode. Figure 6 depicts diurnal cycles averaged over the entire 8 day period. The sum of isoprene and 232 MBO measured by both instruments agrees well (blue and green trace, upper panel). 232 MBO (red) is the dominant biogenic VOC at this site. Isoprene is depicted in black and exhibits typical daytime concentrations of about 200-250 pptv. As expected for light dependent biogenic VOC (BVOC) emissions, the concentration of isoprene and 232 MBO rapidly declines after sunset. The lower panel shows the ratio between isoprene and 232 MBO with an average daytime value of about 0.2. The ratio increases to about 0.5 during night, which could be indicative of different emission patterns between these BVOCs or the influence of non-local isoprene sources. For the 2011 campaign the OH reactivity due to isoprene would amount to up to 40% relative to that of 232 MBO for typical daytime conditions. Future eddy covariance measurements are needed to elucidate emission patterns of these two species in more detail at this site.
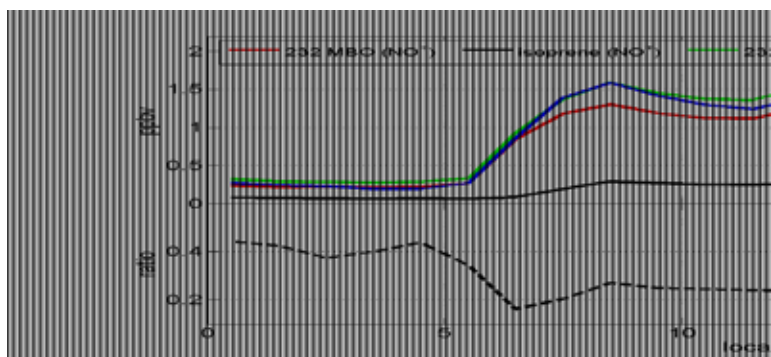
Figure 2: Diurnal concentrations of isoprene and 232MBO using two PTR-TOF-MS instruments (upper panel); one instrument was operated in H3O+ mode depicting 232MBO+isoprene (blue trace); the other instrument was operated in NO+ mode separating 232MBO (red) and isoprene (black). The sum of the two is also plotted for comparison (green trace). The lower panel depicts the ratio between isoprene and 232 MBO.

References

[1] Atkinson, R. Atmospheric chemistry of VOCs and NOx, Atmospheric Environment. 34, 2063–2101 (2000).

[2] Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G. & Wilson J. Organic aerosol and global climate modelling: a review, Atmospheric Chemistry and Physics. 5, 1053–1123 (2005).

[3] Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W.: Proton transfer reaction mass spectrometry: online trace gas analysis at the ppb level, Int. J. Mass Spectrom., 149–150, 609–619, 1995.

[4] Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton transfer- reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass Spectrom., 173, 191–241, 1998.

[5] De Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257, 2007.

[6] Karl, T., Guenther, A., Jordan, A., Fall, R., and Lindinger,W.: Eddy covariance measurements of biogenic oxygenated VOC emissions from hay harvesting, Atmos. Environ., 35, 491–495, 2001.

[7] Fall, R., Karl, T., Jordan A., and Lindinger, W., Biogenic C5 VOCs: release from leaves after freeze-thaw wounding and occurrence in air at a high mountain observatory, Atmospheric Environment 35, 3905-3916, 2001.

[8] Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J. D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res., 109(D18), D18306, doi:10.1029/2004JD004738, 2004.

[9] Warneke, C., de Gouw, J.A., Del Negro, L., Grioude, J., McKeen, S., Stark, H., Kuster, W.C., Goldan, P.D., Trainer, M., Fehsenfeld, F.C., Wiedinmyer, C., Guenther, A.B., Hansel, A., Wisthaler, A., Atlas, E., Holloway, J.S., Ryerson, T.B., Peischl, J., Huey, L.G., Hanks, A.T.C.:Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with biogenic emission inventories, Journal of Geophysical Research, 115, Article Number: D00F18, doi:10.1029/2009JD012445, 2010.

[10] Misztal, P.K., Nemitz, E., Langford, B., Di Marco, C.F., Phillips, G.J., Hewitt, C.N., MacKenzie, A.R., Owen, S.M., Fowler, D., Heal, M.R., Cape, J.N.: Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia, Atmospheric Chemistry and Physics, 11, 8995-9017, 2011.

[11] Goldan, P. D., Kuster, W. C., and Fehsenfeld F. C.: Nonmethane hydrocarbon measurements during the Tropospheric OH Photochemistry Experiment, Journal of Geophysical Research, *102*, 6315−6324, 1997.

[12] Baker, B., Guenther A., Greenberg, J., and Fall, R: Canopy level fluxes of 2-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system, Environmental Science & Technology, 35, 1701-1708, 2001.

[13] Graus, M., Müller, M., and Hansel., A: High Resolution PTR-TOF: Quantification and formula confirmation of VOC in real time, Journal of the American Society for Mass Spectrometry, 21, 1037-1044, DOI: 10.1016/j.jasms.2010.02.006, 2010.

[14] Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Mark, L., Seehauser, H., Schottkowsky, R., Sulzer, P., and Mark, T. D.: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), Int. J. MassSpectrom., 286, 122–128, 2009 (a).

[15] Knighton, W.B., Fornter, E.C., Herndon, S.C., Wood, E.C., Miake-Lye, R.C.: Adaption of a proton transfer reaction mass spectrometer instrument to employ NO^+ as reagent ion for the detection of 1,3 butadiene in the ambient atmosphere, Rapid communications in Mass Spectrometry, 23, 3301-3308, 2009.

[16] Amelynck, C; Schoon, N; Kuppens, T; Bultinck, P; Arijs, E: A selected ion flow tube study of the reactions of H_3O^+, NO^+ and O_2^+ with some oxygenated biogenic volatile organic compounds; Int. Journal of Mass Spectrometry, 247,1-9, 2005.

Acknowledgements

Switch to negative PTR: freons detection in a transportable FT-ICR/MS

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Abstract

Two negative precursors are tested in a small-size transportable FT-ICR/MS. The switch to negative precursor is an important step for the analysis of molecules such as freons. Two precursors HO^- and $O^{-\bullet}$ were studied for a series of halogenated compounds. The products ions (when applicable) and reaction rate constant are reported. Generally, the most convenient precursor (nearly no fragmentation, rapid rate constant, identifiable fragment) for HCFC and HFC is $O^{-\bullet}$ whereas HO^- is most interesting for HCFC and trihalomethanes. CFC and HFO were not shown to react in a simple pattern.

Introduction

Chemical ionization is a powerful tool for identification of traces in a complex mixture when associated to a high resolution mass spectrometer. The classical H_3O^+ precursor is useful for a large amount of compounds [1,2]. Yet this precursor does not ionize the low proton affinity compounds such as alkanes and haloalkanes. A CF_3^+ precursor was developed for freons application [3]. Though ionization was observed, the reaction rate was sometimes low and the fragmentation pattern complicated. Moreover, some fragments were observed to react with water. Such reactions are inconvenient in environmental analysis where air is often saturated with water vapor.

Specific, quantitative analysis of freons in air and seawater was the goal of this study. The haloalkanes are known to be eletrophilic compounds, good reactivity is then to be expected in negative ionization [4,5]. The HCFC and HFC have acidic properties, they may react rapidly with HO^-, a supposed large domain PTR precursor such as H_3O^+ in positive ionization. Another precursor was tested similar to the previous one: $O^{-\bullet}$.

Experimental Methods

The ion-molecule reactions are monitored in a transportable FT-ICR/MS. MICRA (Mobile ICR Analyzer) is a mobile small FT-ICR/MS based on a 1.2 T permanent Halbach magnet. The resolution is better than 0.03 Da in the 2-300 mass range [6].

The reaction is controlled thanks to a sequential introduction of the different gases. First the precursor is ionized. Afterwards the neutral molecule is introduced. Sufficient time is left for the ion-molecule reaction to resume and the pressure to decrease. Pressure and reaction time are controlled by the user. The evolution of the ions ratios versus the reaction time and pressure is monitored to evaluate the reaction kinetic rate constant k_M (cf. Figure 1).

Results

Both precursors HO^- and $O^{-\bullet}$ were studied for a series of halogenated compounds: CFC-12 (CCl_2F_2), HCFC-22 ($CHClF_2$), HFC-23 (CHF_3), HFC-134a (CF_3CH_2F), HFC-143a (CF_3CH_3), HFC-236fa ($CF_3CH_2CF_3$), $CHBr_3$, $CHClBr_2$, $CHCl_2Br$, $CHCl_3$ and HFO-1234yf (CF_3CFCH_2).
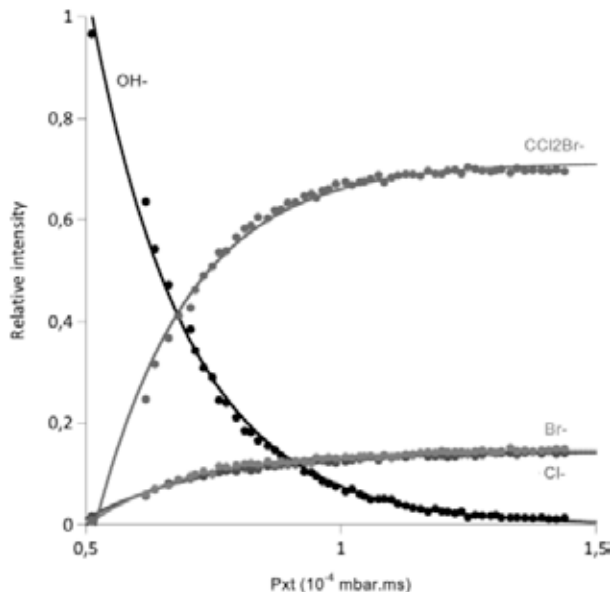
Figure 1: Evolution of the reaction between the precursor HO^- and $CHCl_2Br$. The decrease of the precursor fit resulted in a kinetic rate constant of $k_M = 2{,}89 \ 10^{-9}$ $cm^3.molecule^{-1}.s^{-1}$. Three paths are observed. The predominant path corresponded to the formation of the CCl_2Br^- ion formed by proton transfer reaction.

Discussion

Proton transfer reaction was observed for both precursors for compounds such as trihalomethanes. However the ratio of proton transfer reaction was more important when using the ion hydroxide precursor compared to the oxygen anion. Moreover, both anions reacted as nucleophilic substituent forming the non-characteristic ion X^-. This fragmentation path was observed in particular for HCFC-22 (both anions), for the trihalomethanes (for the oxygen anion) and CFC-12 (for the hydroxide anion). Besides, the oxygen radical anion presented more peculiar reactivity due to its radical reactivity: XO^- formation and H_2^+ abstraction. The former reaction was observed for nearly all CHX_3 molecules (except CHF_3) and CFC-12. The latter reaction formed H_2O by H_2^+ abstraction: this route was observed as the only path for HFC-134a and HFC-236fa. This particular path is then particularly efficient for HFC-134a and HFC-236fa unequivocal detection.

References

[1] Blake, R. S.; Monks, P. S. & Ellis, A. M. Proton-Transfer Reaction Mass Spectrometry Chemical Reviews 109, 861-896, (2009)

[2] Dehon, C.; Gaüzère, E.; Vaussier, J.; Heninger, M.; Tchapla, A.; Bleton, J. and Mestdagh, H. Quantitative analysis of a complex mixture using proton transfer reaction in an FTICR mass spectrometer, International Journal of Mass Spectrometry 272, 29-37, (2008)

[3] Dehon, C.; Lemaire, J.; Héninger, M.; Chaput, A. and Mestdagh, H. Chemical Ionization using CF3+ : Efficient detection of small alkanes and fluorocarbons, International Journal of Mass Spectrometry 299, 113-119, (2011)

[4] Mayhew, C. A.; Peverall, R.; Timperley, C. M. and Watts, P. A selected ion flow tube study of the reactions of OH- with a number of fully and partially halogenated methanes, International Journal of Mass Spectrometry 233, 155-163, (2004)

[5] Staneke, P. O.; J. Kauw, M. Born, S. I. and Nibbering, N. M. M. Low Pressure Gas-phase Reactions of the Atomic Oxygen Radical Anion with Halomethanes Studied Using Fourier Transform Ion Cyclotron Resonance, Rapid Communication in Mass Spectrometry 11, 124-132, (1997)

[6] Mauclaire, G.; Lemaire, J.; Boissel, P.; Bellec, G. and Heninger, M. MICRA: a compact permanent magnet Fourier transform ion cyclotron resonance mass spectrometer, European Journal of Mass Spectrometry 10, 155-162, (2004)

Size-resolved chemical characterization of biogenic nanoparticles by thermal desorption chemical ionization mass spectrometry

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Abstract

Biogenic nanoparticle formation is often referred to as the dominant source of ambient aerosol controlling the number distribution on global scale. Severe societal impacts such as adverse health effects as well as their potential climatic relevance demand comprehensive understanding of the dynamics leading to the formation of airborne nanoparticles. In order to improve current understanding of the species and mechanisms contributing to nanoparticle growth we use a thermal desorption chemical ionization mass spectrometer that allows us to investigate size-resolved chemical composition of particles with diameters down to 10 nm. Data collected during the BEACHON-RoMBAS field campaign in 2011 and laboratory measurements of particles formed from the ozonolysis of α-pinene indicate the importance of this precursor vapor for the growth of ambient biogenic nanoparticles.

Introduction

Atmospheric aerosols have received increasing attention in recent years due to adverse health effects in particle laden air and potentially significant influence on global climate. Depending on particle size, airborne particles may penetrate deeply into lungs and brain [1] causing severe damage in vivo, and directly and/or indirectly interact with solar and terrestrial radiation thereby influencing radiative forcing [2]. One of the most challenging aspects related to aerosol research is the fact that aerosol particles often exhibit highly dynamic behavior which may shift particles from a size where they are non-hazardous or optically irrelevant to a size where they may be hazardous or significantly scatter/absorb light. Understanding and quantifying aerosol sources and dynamical processes is therefore crucial for air quality purposes and climate research.

Besides the direct release of particles through combustion processes, volcano eruptions or sea spray (so-called primary particles), atmospheric particles can also form in situ from precursor gases via nucleation processes and subsequent condensation (secondary organic aerosol, SOA). While it has been known for more than a century that photo-chemically driven new particle formation (NPF) occurs in the atmosphere [3], it was not known until about a decade ago that NPF occurs regularly throughout the troposphere [4]. Globally, biogenic volatile organic compounds (BVOCs) are one of the most important sources of the precursors that lead to NPF. Recent atmospheric measurements and modeling studies have shown that these particles can affect concentrations of cloud condensation nuclei (CCN), and hence the entire hydrological cycle [5, 6]. The effect of biogenic NPF on CCN concentrations and its associated impacts on cloud properties and radiative forcing are the primary motivation for the work presented here.

NPF is often viewed as a two-step process involving nucleation and growth. While the nucleation rate determines the amount of particles formed per unit volume and time, the growth rate relates to the survival probability for freshly formed clusters to grow into larger size particles (typically >10 nm diameter). In order to resolve the lack of understanding of observed growth rates we employ the thermal desorption chemical ionization mass spectrometer (TDCIMS) [7, 8]. TDCIMS has been developed specifically for the task of identifying species and mechanisms responsible for nanoparticle growth. In complementary laboratory and field studies of SOA formation we are able to obtain important insights into the mechanisms and species that control atmospheric nanoparticle growth.

Experimental Methods

The key feature of TDCIMS is its ability to study size resolved particle composition of atmospheric nanoparticles down to 10 nm in diameter at ambient conditions. The TDCIMS is conceptually simple: nanoparticles are charged and size-selected, and then collected on a metal filament. This sampling technique involves low-resolution mobility classification followed by electrostatic precipitation [9]. The low-resolution mobility classification allows a sufficient mass of nanoparticles (1-100 pg) to be collected in sampling times of about 10-15 minutes, while ensuring that sampled particles fall within a well-determined size interval (e.g., 10-15 nm) with no possibility of sample contamination by larger particles, which would account for the majority of the sampled mass. After the sample is collected, the filament is moved into an atmospheric pressure, chemical ionization source region. The filament is resistively heated by passing a constant or time-varying AC current through it, thus heating and desorbing aerosol constituents. Analysis of the desorbed material is then performed by a high-resolution time-of-flight mass spectrometer.
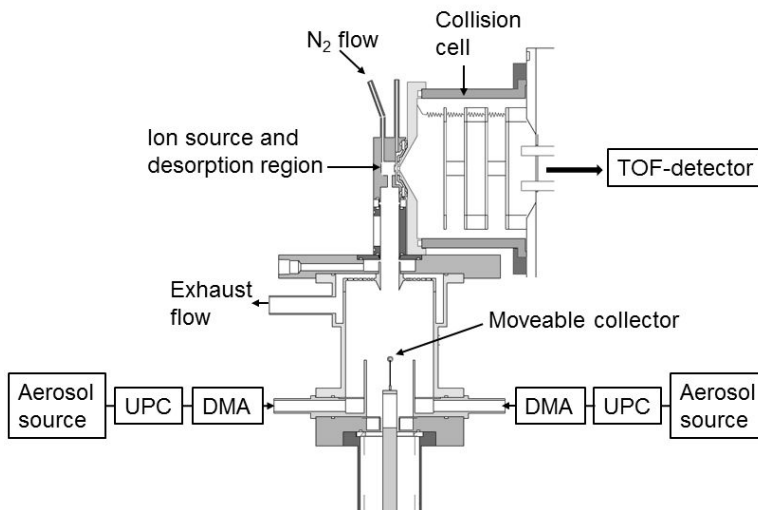
Figure 1: Schematic of TDCIMS inlet. UPC: unipolar charger; DMA: differential mobility analyzer; TOF: time-of-flight.

Results and Discussion

In summer 2011 we participated in the field campaign BEACHON-RoMBAS (**B**io-hydro-atmosphere interactions of **E**nergy, **A**erosols, **C**arbon, **H**$_2$**O**, **O**rganics and **N**itrogen - **Ro**cky **M**ountain **B**iogenic **A**erosol **S**tudy) held at the NCAR operated field site near Woodland Park, Colorado, USA. The site is located in a ponderosa pine dominated forest at an elevation of ~2400m a.s.l. and is partly influenced by emissions from nearby large cities like Colorado Springs and Denver. During the field campaign we observed several NPF events which allowed size-resolved TDCIMS measurements of 20 nm particles. Figure 2 illustrates a negative mass spectrum obtained during an event day from 20 nm particles. The negative signal is clearly dominated by inorganic peaks related to sulfate and nitrate containing compounds. However, a total of 34 ions were identified as organic material, which contributed about 25% to the total aerosol mass.

In complementary laboratory studies we investigated the chemical composition of SOA formed in a flow tube and the NCAR biogenic aerosol chamber. We studied SOA formation from α-pinene + ozone, which is one of the main biogenic SOA formation processes at the BEACHON site. The chemical analysis yielded a substantial amount of species showing clear size dependence [10]. While particles with sizes below 20 nm were characterized by enhancements of carboxylic acids, particles in the order of 40 nm were dominated by carbonyl containing compounds. Interestingly, all of the 34 identified organic ions from the field study were also detected in the α-pinene initiated SOA. It can thus be expected that α-pinene is an important precursor contributing to atmospheric biogenic nanoparticle growth.
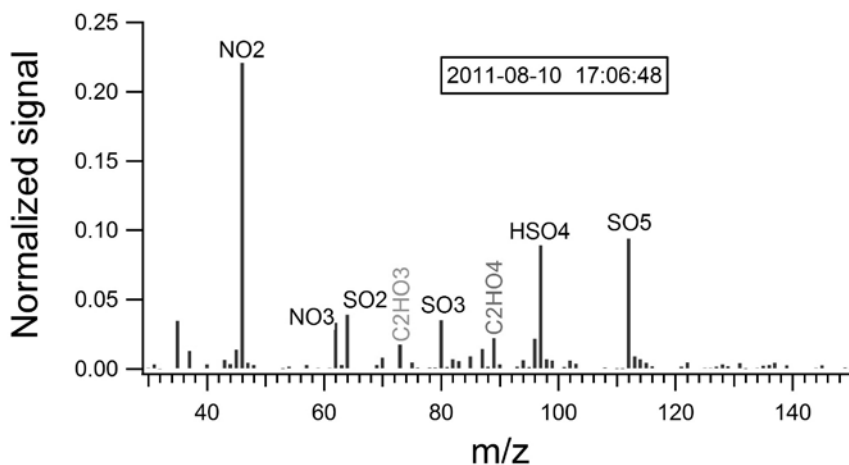
Figure 2: Unit-mass resolution mass spectrum (negative polarity) from 20 nm particles.

References

[1] G. Oberdörster, E. Oberdörster, and J. Oberdörster, Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. Environ. Health Perspec., 113, 823-839 (2005).

[2] P. Forster, et al. 2007, Changes in Atmospheric Constituents and in Radiative Forcing. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[3] J. Aitken, On some nuclei of cloudy condensation, Trans. Royal Soc. Edinburgh, 39(3), 15-25 (1898).

[4] M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, and P. H. McMurry, Formation and growth rates of ultrafine atmospheric particles: A review of observations, J. Aerosol Sci., 35, 143, 2004.

[5] D. V. Spracklen, K. S. Carslaw, M. Kulmala, V.-M. Kerminen, S. L. Sihto, I. Riipinen, J. Merikanto, G. W. Mann, M. P. Chipperfield, A. Wiedensohler, W. Birmili, and H. Lihavainen, Contribution of particle formation to global cloud condensation nuclei concentrations, Geophys. Res. Lett. 35, L06808 (2008).

[6] V.-M. Kerminen, H. Lihavainen, M. Komppula, Y. Viisanen, and M. Kulmala, Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation, Geophys. Res. Lett. 32, L14803 (2005).

[7] D. Voisin, J. N. Smith, H. Sakurai, P. H. McMurry, and F. Eisele, Thermal desorption chemical ionization mass spectrometer for ultrafine particle chemical composition, Aerosol Sci. Technol. 37, 471-475 (2003).

[8] J. N. Smith, and G. J. Rathbone, Carboxylic acid characterization in nanoparticles by thermal desorption chemical ionization mass spectrometry, Int. J. Mass Spectrom. 274, 8-13 (2008).

[9] P. H. McMurry, A. Ghimire, H. K. Ahn, H. Sakurai, K. Moore, M. Stolzenburg, and J. N. Smith, Sampling Nanoparticles for chemical analysis by low resolution electrical mobility classification, Environ. Sci. Technol. 43, 4653-4658 (2009).

[10] P. M. Winkler, J. Ortega, T. Karl, L. Cappellin, H. R. Friedli, K. Barsanti, P. H. McMurry, and J. N. Smith, Identification of the biogenic compounds responsible for size-dependent nanoparticle growth, Geophys. Res. Lett., 39, L20815.

Development of a compact PTR-ToF-MS for Suborbital Research on the Earth's Atmospheric Composition

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Abstract

DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) is a multi-year NASA field campaign to improve the use of satellites to monitor air quality: http://discover-aq.larc.nasa.gov/. In the frame of DISCOVER-AQ, NASA deploys the P3-B Airborne Science Laboratory for in-situ measurements of atmospheric pollutants over selected areas in the U.S. affected by poor air quality. Airborne observations of trace hydrocarbons by PTR-MS shall provide important information on air pollution sources and processes which will be used to improve the interpretation of space-borne observations of air pollutants by current and future satellites.

Conventional airborne PTR-MS instruments include quadrupole mass spectrometers which typically detect a set of 10 trace gases with a 1-second signal integration period for each species. This transfers into an overall time resolution of 10 seconds or a nominal 1000 m horizontal and 100 m vertical spatial resolution for airborne measurements. This is often too low when operating over urban areas, in the proximity of point sources and during extensive vertical profiling, i.e. when it is essential to be able to resolve large gradients over very small distances.

In this project funded by the "Austrian Space Applications Programme 8" (FFG-ALR, BMVIT), a consortium composed by the University of Innsbruck and Ionicon Analytik developed, constructed and validated a prototype compact PTR-ToF-MS instrument for deployment on NASA's airborne science platforms. The light-weight, low mass resolution orthogonal acceleration TOF-MS generates full mass spectrum information at 1-second time resolution with typical 2σ-detection limits in the 0.1-to-0.2 ppbV range. The prototype will be deployed on the NASA P3-B during the January-February 2013 DISCOVER-AQ mission which will investigate winter-time air pollution in the Central California Valley.

In my talk, I will describe the prototype instrument, provide performance details and present data from the first field deployment.

Applications in Environmental Science

Measurement of H_2S by PTR-MS: Experiences and implications

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Abstract

Online methods that are unbiased by sampling are relevant for measuring fluctuating emissions of H_2S from various sources. In this work, the application of PTR-MS for measuring H_2S is investigated. Since proton transfer from H_3O^+ is only slightly exothermic, significant backwards transfer causes a humidity dependency of the sensitivity. It is demonstrated that this can be overcome by a humidity dependent calibration. Another consequence is that the detection limit is in the low ppb range (2-5 ppb) rather than the usual ppt range and is also dependent on humidity. Nevertheless, PTR-MS can be a very useful online tool for investigating e.g. H_2S emissions and H_2S emission abatement in many situations where H_2S is present at ppb levels. Other ionization methods (O_2^+ and NO^+) were found not to be useful for H_2S detection.

Introduction

Hydrogen sulfide (H_2S) is ubiquitous in the atmosphere with a range of different emission sources, such as wetlands, soil, volcanoes, oceans, automobiles, oil processing and livestock production [1,2,3]. Due to its relatively low water solubility and potential surface oxidation [4], emissions of H_2S may be very fluctuating with short term spikes under specific conditions [5] and thus total emissions are difficult to assess. In relatively low concentrations, H_2S has been linked to respiratory disease [6] and odor nuisance caused by intensive livestock production [3].

Despite its numerous sources and impacts, relatively few studies are dealing with the emission strengths and the importance of different sources of H_2S in comparison with other sulfur compounds [2]. Part of this lack of knowledge is ascribed to analytical challenges in measurements of H_2S, since it is a reactive compound and therefore difficult to collect in sampling enclosures and on sorbent traps.

Measuring of H_2S by means of PTR-MS is interesting for the following reasons: 1) PTR-MS is an excellent method for measuring reduced organic sulfur compounds, which in many cases have the same sources as H_2S, and thus only one method is necessary for covering this compound class, 2) no sample collection is needed in PTR-MS, which prevents degradation of H_2S during sampling and storage, and 3) Due to the online measurement ability of PTR-MS, fluctuating concentrations of H_2S can be monitored. Due to its proton affinity being only slighter higher than water, however, the sensitivity towards H_2S will be influenced by air humidity.

Experimental Methods

A high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was applied for measuring the removal of odorants in the biofilter. The PTR-MS is based on chemical ionization of compounds by protonated water (H_3O^+) in a drift tube and subsequent detection of ionized compounds in a quadrupole mass spectrometer. In the presented work, the PTR-MS was operated under standard

ion drift tube conditions applying a total voltage of 600 V and maintaining the pressure in the range of 2.1 – 2.2 mbar (E/N value ~135 Td). Additional tests of detection of H_2S by using O_2^+ and NO^+ as ionization agents were also attempted.

Different concentrations of H_2S in air were obtained by diluting certified gas standards containing ~5 ppm H_2S in N_2 with purified (charcoal filtered) dry (dew point: -30°C) air. Mass flow controllers were used for dilution and great care was taken in order to avoid loss of H_2S in the mass flow controllers by waiting until a stable output of H_2S could be measured (up to 15 minutes after starting up). A variable fraction of the dilution air was humidified by an impinger equipped with a glass frit for bubble creation. Humidity levels from ~0% up to ~85% were obtained.

A simple alternative method was to collect a diluted sample of H_2S (at a known concentration) in a Tedlar sampling bag and then add liquid water through a septum by a syringe. By measuring during water evaporation, H_2S data at fixed concentration and variable humidity is quickly obtained.

During application of PTR-MS for measuring H_2S, similar setups were used. Some of the results have been reported elsewhere, e.g. [5,7,8]. Comparisons of PTR-MS measurement and measurements by GC with sulfur chemiluminescence detection and by a column trapping chemiluminescence method shows generally good agreement between the methods [8,9].

Results
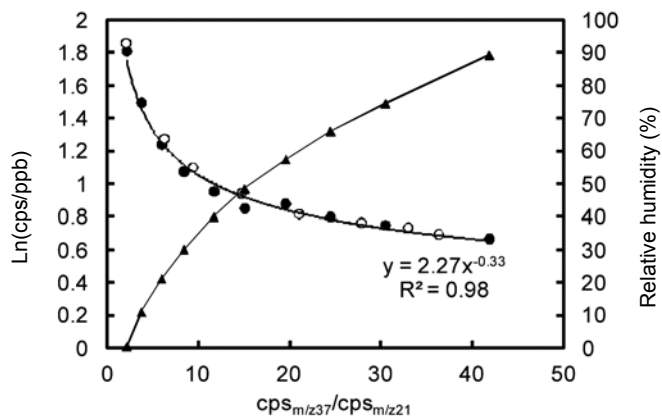
Figure 1: Plot of the natural logarithm of the sensitivity as a function of the relative abundance of m/z 37. Results are shown for two concentrations, 277 ppb (○) and 830 ppb (●). Relative humidity is included for comparison (▲).

An example of a graphical representation of the humidity dependency is presented in Figure 1. The natural logarithm of the sensitivity is expressed as a function of the relative abundance of the primary water cluster ion (m/z 37/m/z 21), which is related to the relative humidity. An empirical relation is fitted and can be used to correct data based on the relative abundance of m/z 37. As can be seen, the ratio of m/z 37 to m/z 21 is very well correlated with humidity, although the relationship is not linear. The humidity dependent calibration curve does not appear to be influenced by H_2S concentration (in the ppb range). The ratio of water clusters to primary ion

(m/z19 = 500 × m/z21) exceeds 5% at a relative humidity of ~70% (at 22°C), and measurements at humidity above this level should in general be carried out with great care, i.e. dilution with dry air may be an advantage.
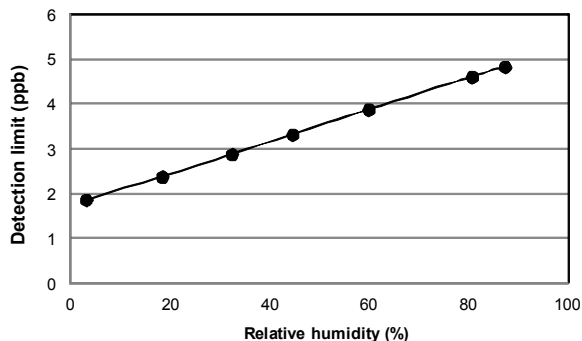
Figure 2: Plot of the estimated detection limit as a function of relative humidity. The data is based on a signal detection limit of 9 cps and the relationship between relative humidity and sensitivity presented in Figure 1.

The detection limit of the method also depends on humidity. A signal detection limit of 9 cps (counts per second) was estimated from the background noise level (3 times the standard deviation of subsequent blank signals) at an ion dwell time of 500 msec. The detection limit in units of ppb was then estimated from the data in Figure 1. The relationship between detection limit and relative humidity (at room temperature) is presented in Figure 2. As can be seen, the detection limit ranges from ~2 in dry conditions to ~5 in humid conditions.

Discussion

It is demonstrated that PTR-MS is clearly useful for detection and quantification of H_2S. The main limitation is that the sensitivity as well as the detection limit is humidity dependent and that the detection is high. The reduced sensitivity is due to the backwards reaction of protonated H_3S^+ being important due to the low exothermicity. The detection limit may be decreased by increasing the dwell time, but is nevertheless higher than for most other compounds measured by PTR-MS. PTR-MS is very useful for measuring fluctuating emissions of H_2S from sources such as livestock waste and livestock production facilities in which concentrations of >100 ppb often is encountered. Our research group has used the method for investigating e.g. surface processes in relation to H_2S emissions from manure and for optimization of air treatment technologies for livestock production facilities.

A preliminary test of the application of NO^+ and O_2^+ showed that these ionization agents are not readily suitable for detection of H_2S despite the fact that the ionization energy of H_2S is lower than that of O_2 and therefore should undergo charge transfer. The reason for this is that the H_2S^+ ions formed from O_2^+ react with H_2O by proton transfer ($k = 8 \times 10^{-10}$ cm^3 s^{-1}) [10].

References

[1] J. H. Seinfeld and S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, (1997)

[2] S. F. Watts, The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, Atmospheric Environment 34, 761-779 (2000)

[3] A. Feilberg, D. Z. Liu, A. P. S. Adamsen, M. J. Hansen, and K. E. N. Jonassen, Odorant Emissions from Intensive Pig Production Measured by Online Proton-Transfer-Reaction Mass Spectrometry, Environmental Science & Technology 44, 5894-5900 (2010)

[4] D. A. Nielsen, L. P. Nielsen, A. Schramm, and N. P. Revsbech, Oxygen Distribution and Potential Ammonia Oxidation in Floating, Liquid Manure Crusts, Journal of Environmental Quality 39, 1813-1820 (2010)

[5] D. Liu, A. Feilberg, A. P. S. Adamsen, and K. E. N. Jonassen, The effect of slurry treatment including ozonation on odorant reduction measured by in-situ PTR-MS, Atmospheric Environment 45, 3786-3793 (2011)

[6] D. Campagna, S. J. Kathman, R. Pierson, S. G. Inserra, B. L. Phifer, D. C. Middleton, G. M. Zarus, and M. C. White, Ambient hydrogen sulfide, total reduced sulfur, and hospital visits for respiratory diseases in northeast Nebraska, 1998-2000, Journal of Exposure Analysis and Environmental Epidemiology 14, 180-187 (2004)

[7] A. Feilberg, D. Z. Lu, A. P. S. Adamsen, M. J. Hansen, and K. E. N. Jonassen, Odorant Emissions from Intensive Pig Production Measured by Online Proton-Transfer-Reaction Mass Spectrometry, Environmental Science & Technology 44, 5894-5900 (2010)

[8] M. J. Hansen, D. Z. Liu, L. B. Guldberg, and A. Feilberg, Application of Proton-Transfer-Reaction Mass Spectrometry to the Assessment of Odorant Removal in a Biological Air Cleaner for Pig Production, Journal of Agricultural and Food Chemistry 60, 2599-2606 (2012)

[9] M. J. Hansen, K. Toda, T. Obata, A. P. S. Adamsen, and A. Feilberg, Evaluation of Single Column Trapping/Separation and Chemiluminescence Detection for Measurement of Methanethiol and Dimethyl Sulfide from Pig Production, Journal of Analytical Methods in Chemistry (2012)

[10] P. Spanel and D. Smith, Quantification of hydrogen sulphide in humid air by selected ion flow tube mass spectrometry, Rapid Communications in Mass Spectrometry 14, 1136-1140 (2000)

VOCs in the Uintah Basin, Utah – First measurements with the new Ultra-Light-Weight PTR-MS

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Abstract

The ULW-PTR-MS (Ultra-Light-Weight Proton-Transfer-Reaction Mass Spectrometer) is a newly built system that is particularly compact and lightweight through the design of custom-built electronics and a new vacuum system. Originally designed for the use onboard the research aircraft HALO (see contribution by Zahn et al.) it was fielded for the first time during UBWOS 2012 (Uintah Basin Winter Ozone Study) – an air quality study of the wintertime ozone exceedances in the Uintah basin that have been linked to the oil and natural gas production. The center during this campaign was the Horsepool field site, which was constructed on a former well pad in the middle of the oil and gas fields in the backcountry of the Uintah Basin in northeastern Utah.
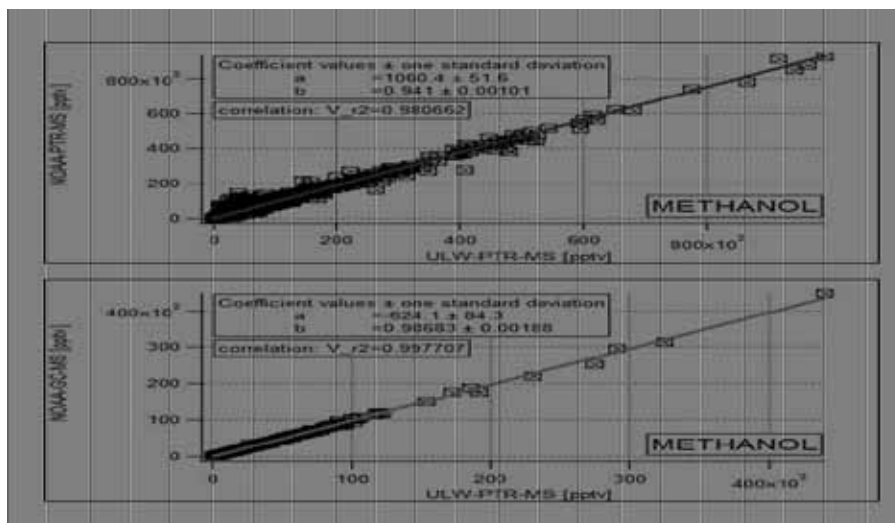
Direct comparisons and measurements between ULW-PTR-MS and the existing NOAA-PTR-MS (de Gouw & Warneke 2007) and NOAA-GC-MS (Goldan 2004) instruments have been performed at Horsepool. The agreement between the three instruments was very good, see Fig. 1 for methanol, which attests to the accuracy of the new ultra-lightweight system.

Total mass spectra (between 20 and 170 amu) were measured to determine the VOCs present in the basin, as well as inside plumes to determine the full individual composition of different sources. Overlaying these spectra with laboratory measurements of oil samples verify that the appearing peaks in the atmospheric spectrum are especially caused by alkanes, cycloalkanes and aromatics – major constituents of fossil oil.

The small size and light weight of the ULW-PTR-MS allowed it to be installed in the Mobile Lab (NOAA Global Monitoring Division Mobile Lab) halfway through the campaign to make VOC measurements near point sources in the basin. Downwind of gas and oil wells mixing ratios of up to several tens of ppbv´s of compounds such as benzene or C8-aromatics were observed. Higher mixing ratios of up to several ppmv were observed downwind from a well that had recently been hydraulically fractured and that used a flow-back pond for containing produced water (Fig. 2).
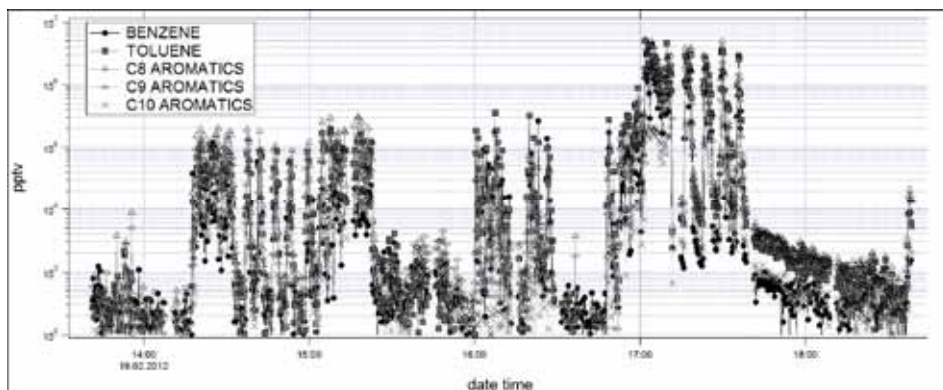
Figure 2: Time series of aromatics (benzene, toluene, C8, C9 and C10) on the 2012-02-19 drive through the basin; very high mixing ratios downwind of flowback site (17:00 – 17:35)

BVOC Emissions from Corn and their Influence on Reactive Nitrogen

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Abstract

Corn plants emit significant amounts of volatile organic compounds (VOCs) with methanol being the largest emission and smaller emissions of other VOCs such acetone, acetaldehyde, monoterpene and dimethyl sulfide (DMS). During the day VOCs mainly react with hydroxyl radicals but at night they can react with nitrate radicals (NO_3). DMS was found to be a significant contributor to the nitrate reactivity over a cornfield in Colorado and our data suggests that in areas with high corn acreage that are downwind of urban areas and other significant NO_x sources terrestrial DMS may be the dominant sink for reactive nitrogen.

Introduction

In the United States large amounts of corn are grown for the use as animal feed, for the food industry and for the production of fuel ethanol. In 2012 the acreage of corn planted was 390,000 km^2 covering over 5% of the contiguous US land surface [1]. In recent years about 40% of the corn crop was used to produce fuel ethanol to cover nearly 10% of the gasoline used by cars [1-3].

Plants emit substantial amounts of volatile organic compounds (VOCs) into the atmosphere where they may contribute to the atmospheric reactivity, form ozone during the course of their oxidation or fuel aerosol formation and aerosol growth. They also may contribute to the formation of peroxyacylnitrates, or influence the nighttime chemical processing of nitrogen oxides by reacting with nitrate radicals. Composition and emission rates of those biogenic VOCs vary strongly between plant species and are governed by phenological factors (e.g. stage of plant development), physiological factors (e.g. photosynthesis rate, stomatal conductance, …) and environmental factors (temperature, solar radiation, water availability, stress factors, …). Crops have been thought to be low emitters of VOCs, but considering the abundance of agricultural ecosystems in parts of the US they may influence the air chemistry on local and regional levels.

Experimental Methods

The BioCORN 2011 field experiment took place in summer 2011 to look at ecosystem fluxes of VOCs from a cornfield in Fort Collins, Colorado, during the period of rapid biomass increase and

Experimental Methods

The BioCORN 2011 field experiment took place in summer 2011 to look at ecosystem fluxes of VOCs from a cornfield in Fort Collins, Colorado, during the period of rapid biomass increase and development of flowers and ears. Eddy covariance, soil and leaf cuvette measurements using various instruments including PTR-MS, NI-PT-CIMS and GC-MS were used to determine fluxes of VOCs, quantify emission rate in relation to physiological parameters and specify the identity of the compounds in the ambient air over the cornfield. A number of inorganic species were also measured during the BioCORN study.

Results and Discussion

Here we focus on VOC fluxes measured by PTR-MS using the disjunct eddy covariance approach and we use GC-MS data from soil and leaf enclosures as well as ambient air samples to substantiate the compound identification. The highest VOC fluxes from the cornfield were found for methanol with a distinct diurnal pattern of fluxes showing maximum emissions around noon and low emission rates or deposition during the night. Other oxygenated VOC fluxes such as acetone and acetaldehyde were an order of magnitude smaller than those of methanol, and nighttime fluxes were less frequently detectable. Small amounts of monoterpenes were emitted during the day with camphene being identified by GC-MS sampling from a leaf cuvette as the only significant monoterpene emission from corn. Dimethyl sulfide (DMS), measured by PTR-MS at m63, also showed a distinct diurnal pattern in the ecosystem flux. The GC-MS enclosure data identified corn leaves as the dominant contributor to the ecosystem flux of DMS and only small amounts coming from the soil. Moreover, the DMS emissions from the leaves correlate well with stomatal conductance (R^2 = 0.89) and with net assimilation of CO_2 (R^2 = 0.94). The eddy flux data and cuvette data suggest that corn contributes significantly to the abundance of ambient DMS, which was several tens of pptv during the day and increasing to about 100 pptv at night as measured by both PTR-MS and GC-MS. Monoterpenes were also present in the ambient air above the cornfield, with pinenes (not emitted from corn) accounting for the largest part and only a small fraction of camphene. The largest part of the monoterpenes may have been emitted from other sources (e.g. pine forests in the nearby Rocky Mountains) and transported to the field site. Budgets for the loss of NO_3 to VOCs were calculated from the bimolecular reaction rate coefficients (k_i, cm^3 molecule^{-1} s^{-1}) for NO_3 with respect to each VOC and the time series of the measured mixing ratio (converted to concentration, molecule cm^3) for each VOC. A suite of 39 VOCs measured by GC-MS was used for this purpose. Also included in the budget is the loss of NO_3 due to heterogeneous uptake of N_2O_5 to aerosol. The overall NO_3 reactivity (or first order loss rate coefficient, s^{-1}) is then calculated as the sum of the VOC and heterogeneous reactivities for NO_3.

$$k(NO_3) = \sum_i k_i[VOC_i] + K_{eq}[NO_2]k(N_2O_5)$$

Averaged over nighttime data only (defined as solar zenith angle > 90°) DMS accounts for one fifth and the sum of monoterpenes for about half of the average NO_3 reactivity. Camphene, the only monoterpene emitted from corn, however, accounts only marginally to the nitrate reactivity. This suggests that DMS may be a significant sink for reactive nitrogen in areas with high corn acreage that are downwind of urban areas and other significant NO_x sources.

References

[1] National Agricultural Statistics Service (NASS), Acreage Report 2012 released 6/29/2012

[2] US Energy Information Administration (EIA), Annual Energy Review released 9/27/2012

[3] R. Soto, I. Russell, N. Narendranath, R. Power, and K. Dawson, Estimation of Ethanol Yield in Corn Mash Fermentations Using Mass of Ash as a Marker, Journal of the Institute of Brewing, 111(2), 137-143, (2005).

Prediction of odor from animal production based on odorants measured by PTR-MS

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Abstract

Development of odor reduction technologies for animal production requires a reliable method that can be used to estimate the effect on odor. The aim of the present study was to demonstrate the potential of odor prediction based on odorants measured by PTR-MS. A semi-field method was applied by which both odor concentration measured by olfactometry and odorants were measured in sample bags collected from pig production facilities. The results demonstrate that prediction of odor based on measurements by PTR-MS is a feasible method. Hydrogen sulfide, methanethiol, trimethylamine and 4-methylphenol were identified as the odorants with the largest influence on the prediction of odor from pig production, whereas carboxylic acids only have a limited influence. In conclusion, prediction of odor based on measurements by PTR-MS is a promising method that can be used to develop odor reduction technologies, but the method has to be evaluated with on-site measurements. Based on the results from the present study a mobile laboratory is being developed at Aarhus University, Department of Engineering for on-site measurements in animal production facilities. The objective of the new project is to develop a more precise prediction model for pig production and to identify the most important odorants.

Introduction

Odor from animal production can be a great nuisance to people living in the vicinity of the production facilities and it is necessary to develop odor reduction technologies. However, the development of odor reduction technologies requires a reliable method to estimate the effect on odor. At the moment odor from animal production is measured by olfactometry [1] where dilution-to-threshold is determined by human noses. This method has a number of drawbacks including loss of odorants during storage [2,3] and a large variation associated with the use of human noses [4]. It is therefore of great interest to develop a method based on chemical measurements of odorants that can be used to estimate the odor emission from animal production and the effect of an odor reduction technology. The aim of the present study was to evaluate the potential of odor prediction based on odorants measured by PTR-MS.

Experimental Methods

Air samples were collected from four experimental pig production facilities with growing-finishing pigs. Seventy two pairs of air samples were collected in 30-L sample bags (Nalophan NA 0.20 μm, OLFAtec GmbH, Kiel, Germany). One half of the samples were sent to an odor laboratory (Danish Meat Research Institute, Roskilde, Denmark) for analysis of the odor concentration (OU_E/m^3) by olfactometry and the other half of the samples were analyzed by PTR-MS (Aarhus University, Foulum, Denmark). The samples were analyzed approximately 24 h after sampling. The PTR-MS was operated under standard ion drift tube conditions applying a total voltage of 600 V and maintaining the pressure in the range of 2.1-2.2 mbar (E/N value ~135 Td).

The temperature of the drift tube was controlled at 60 °C and the inlet sampling flow was adjusted to ca. 70 mL min^{-1}. The measured odorants included sulfur compounds, carboxylic acids, amines, ketones, phenols and indoles. The measurements were performed as single ion monitoring of 21 ions between m/z 35 to m/z 132 with each ion being detected for 500 ms during each cycle. A total of 30 cycles were measured during each measurement on the bags. Between the measurements of the bags, instrumental background was measured on room air purified for hydrocarbon contaminants with a Supelpure™ HC filter (Supelco, Bellefonte, Pennsylvania, USA).

Results and Discussion

A partial least squares (PLS) regression model was used to predict the odor concentration based on the concentration of odorants measured by PTR-MS, see Figure 1. Based on the root mean square error for the cross validated model, it was shown that the optimum PLS model was obtained with three PLS components. The PLS model with three PLS components accounted for 55% of the variation in the odor concentration and 82% of the variation in the concentration of odorants. The regression coefficients for the individual odorants demonstrated that carboxylic acids had regression coefficients close to zero and only a limited impact on the prediction of odor from pig production. Furthermore, carboxylic acids have quite high odor threshold values [5] compared to the concentration level measured in pig production and these compounds are not considered to be important odorants from pig production. The odorants with the highest regression coefficients were hydrogen sulfide, methanethiol, acetone, trimethylamine and 4-methyphenol. Except for acetone these odorants all have quite low odor threshold values compared to the concentration level measured in pig production and are considered to be significant odorants. More detailed information about the study can be found in Hansen et al. (2012) [6].
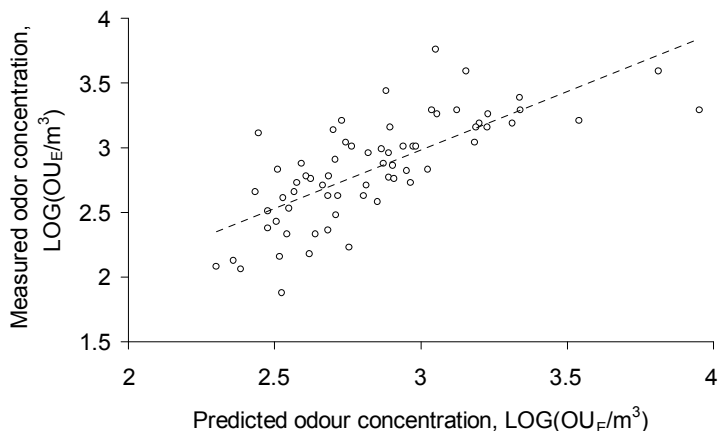
Figure 1. Measured odor concentration (OUE/m3) from pig production facilities as a function of predicted odor concentration based on odorants measured by PTR-MS. After: Hansen et al. (2012)[6].

References

[1] National Agricultural Statistics Service (NASS), Acreage Report 2012 released 6/29/2012

[2] US Energy Information Administration (EIA), Annual Energy Review released 9/27/2012

[3] R. Soto, I. Russell, N. Narendranath, R. Power, and K. Dawson, Estimation of Ethanol Yield in Corn Mash Fermentations Using Mass of Ash as a Marker, Journal of the Institute of Brewing, 111(2), 137-143, (2005).

Organic aerosol analysis with thermal-desorption (TD-) PTR-MS

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Abstract

The TD-PTR-MS technique has been developed about 4 years ago at Utrecht University, the Netherlands, initially in collaboration with the Max Planck Institute for Chemistry, Germany. Since then the technique has been applied in several field campaigns and is proven to detect hundreds of organic (as well as some inorganic) species in aerosols at an approximately hourly time resolution. The detailed chemical information obtained with PTR-TOF technology is valuable information to elucidate processes of secondary organic aerosol (SOA) formation.

Introduction

Health issues and climate effects are the two fundamental reasons why carbonaceous aerosol pollution is of concern. Many organic species in aerosols are carcinogenic and/or the cause of respiratory illnesses [1,2].

Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometry (TD-PTR-MS), based on a novel combination of an aerosol inlet previously developed for in situ thermal desorption GCMS [3] and proton-transfer reaction mass spectrometry (PTR-MS) to evaluate both the composition and volatility of organic aerosol. The conceptual idea is similar to the method described by Thornberry et al. [4]. The TD-PTR-MS instrument fills a niche because it allows for aerosol measurements at a time resolution below 1 hour, with detailed and comprehensive physicochemical information and an excellent detection limit. Therefore the TD-PTR-MS has a high potential to elucidate chemical processes that transform fresh aerosol (either primary emissions or first-generation secondary aerosol observed in smog-chamber experiments) to the highly oxidized aerosol that is typically observed in the field.

Experimental Methods

The TD-PTR-MS has been described by Holzinger et al [5]. Since 2009 we used an instrument with a high mass resolution time-of-flight mass-spectrometer and a dual aerosol inlet which was in principal operated as described in Holzinger et al [6]. The setup is shown in Figure 1a. Briefly, ambient particles in the 0.07–2 μm size range are collected on a Collection-Thermal-Desorption (CTD) cell. Aerosol compounds are thermally released from the CTD-cell by ramping the temperature up to 350ºC in seven steps of 50ºC. Every temperature step is completed in three minutes and consists of a ramp and a dwell period of approximately 2 and 1 minutes, respectively. A nitrogen carrier gas is used to transport evaporating aerosol compounds through heated transfer lines (200ºC) from the CTD cell to the detector, which is a PTR-TOF 8000 (Ionicon Inc. Austria). Figure 1b shows the timeline of m/z 59.049 as an example. The temperature steps of the CTD cell can be seen very clearly by a sharp increase, peak mixing ratio, and a sharp decrease after the bulk of material, which can be volatilized at a temperature level, has been transported to the PTR-MS. In this manner thermogram information is obtained for each observed aerosol species.

The operation of the system is fully automated and follows a fixed scheme which can be seen by the green, red, and brown bars below the x-axis in Figure 1b. One cycle can be completed in 90 minutes and includes the analysis of the first (i) and second (ii) aerosol inlet, (iii) the analysis of ambient air (two periods of 10 minutes), and (iv) the analysis of gas phase background (two periods of 5 and 10 minutes, respectively), which is accomplished by leading ambient air through a platinum catalyst operated at 350ºC. The aerosol background is measured every other run by sampling through a Teflon membrane filter (Zefluor 2.0 µm, Pall Corp.) that removes the particles from the air stream.
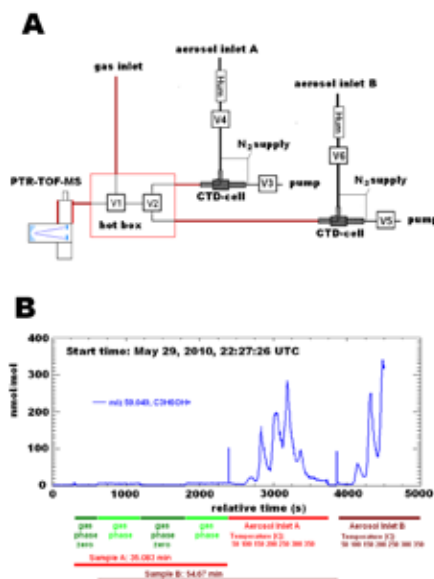
Figure 1: Basic setup and operation of the TD-PTR-MS during the CalNex campaign in California during summer 2010.

Results and discussion

Detection of aerosol species

The aerosol signal is computed for all detected species by subtracting the signal of the filtered ambient air sample from the signal of the unfiltered sample. The closest filtered sample of the respective aerosol inlet is used as background and the subtraction is done point for point for each temperature level. The computed aerosol signal of a detected species is considered significantly enhanced if its mean value is at least 3 times the standard deviation of the background signal for at least 2 temperature levels. Several hundreds of detected species typically fulfill this criterion and are thus detected in aerosols.

Figure 2 shows all 1210 mass peaks detected during a field campaign at the Mt Sonnblick observatory in the Austrian alps in summer 2009 [6]. The hydrocarbons clearly stand out as straight line in the Figure. The insert enlarges the C_{29} hydrocarbons. Note that for these hydrocarbon series typically the two most abundant isotopologues were detected (i.e. the one containing only ^{12}C atoms, and the species containing one ^{13}C atom.). To the left and right of the C_{29} line are the C_{28} and the C_{30} lines, respectively. Oxygenated compounds are below the

hydrocarbons on the graph because they are typically lighter (m(CH4)-m(O) = 36.4 mDa). Peaks printed in blue or cyan were significantly enhanced in aerosols. Peaks printed in blue and black were identified by their empirical formula; peaks printed in cyan and grey were only identified by their molecular weight. Note that most high molecular weight hydrocarbon signals were not detected in aerosols but due to instrumental background.
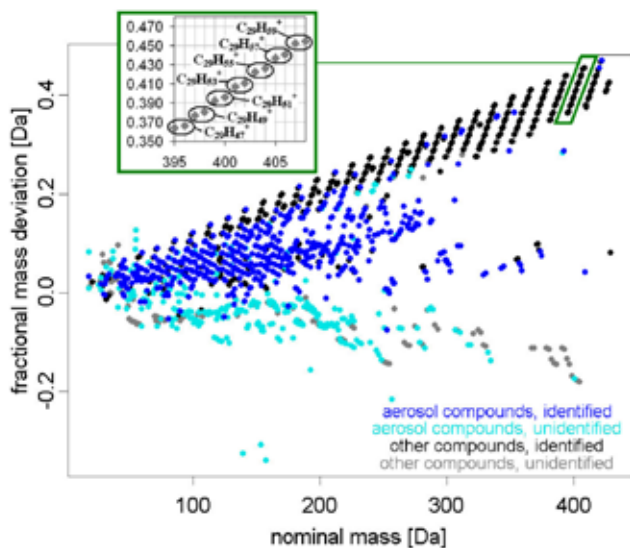
Figure 1: Detected mass peaks during field measurements at the Mt Sonnblick observatory, Austria [6].

TD-PTR-MS aerosol measurements during the CalNex 2010 campaign

In the framework of the California Research at the Nexus of Air Quality and Climate Change (CalNex) 2010 project a field site was operated on the campus of the California Institute of Technology (Caltech) in Pasadena (34.1408 °N, 118.1223 °W, 230 m ASL), approximately 18 km northeast of downtown Los Angeles. Measurements were made from 15 May through 16 June 2010.

Figure 3 summarizes some of the findings from the CalNex campaign. For most compounds the background signal of the filtered samples was significantly lower than the unfiltered samples. Surprisingly nitrogen compounds constituted more than 20% of the detected aerosol mass, roughly half of this was due to compounds with one and two nitrogen atoms, respectively. Evaluating the thermogram information reveals that the N_1- and N_2- compounds exhibit different physical properties. While N_2-compounds evaporate at lower temperatures the N_1 compoounds are significantly less volatile suggesting that the latter group is more processed.

	Number of Species	Median Concentration[1] [ng m^{-3}]
All organics (identified by empirical formula)	327	3700
Hydrocarbons	73	480
Oxygenated organics	123	2400
Organosulfates	20	70
N$_1$-Organics	78	410
N$_2$-Organics	33	350
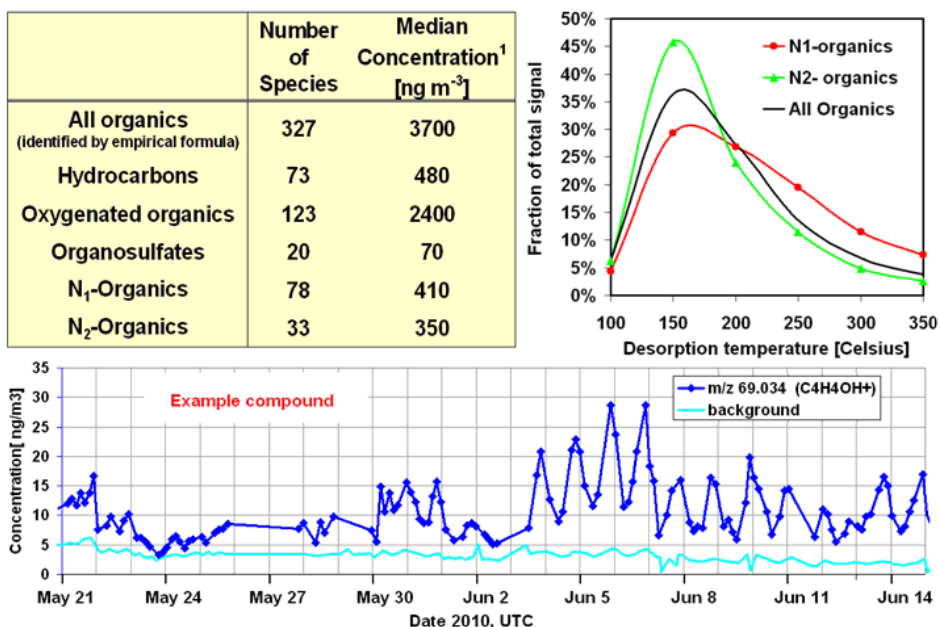
Figure 3: Overview of results from the CalNex 2010 campaign.

References

[1] Mauderly, J. L., and Chow, J. C.: Health effects of organic aerosols, Inhalation Toxicology, 20, 257-288, (2008).

[2] Poschl, U.: Atmospheric aerosols: Composition, transformation, climate and health effects, Angewandte Chemie-International Edition, 44, 7520-7540, (2005).

[3] Williams, B. J., Goldstein, A. H., Kreisberg, N. M., and Hering, S. V.: An in-situ instrument for speciated organic composition of atmospheric aerosols: Thermal Desorption Aerosol GC/MS-FID (TAG), Aerosol Science and Technology, 40, 627-638, (2006).

[4] Thornberry, T., Murphy, D. M., Thomson, D. S., de Gouw, J., Warneke, C., Bates, T. S., Quinn, P. K., and Coffman, D.: Measurement of Aerosol Organic Compounds Using a Novel Collection/Thermal-Desorption PTR-ITMS Instrument, Aerosol Science and Technology, 43, 486-501, (2009).

[5] Holzinger, R., Williams, J., Herrmann, F., Lelieveld, J., Donahue, N. M., and Rockmann, T.: Aerosol analysis using a Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometer (TD-PTR-MS): a new approach to study processing of organic aerosols, Atmospheric Chemistry and Physics, 10, 2257-2267, (2010).

[6] Holzinger, R., Kasper-Giebl, A., Staudinger, M., Schauer, G., and Rockmann, T.: Analysis of the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-TD-PTR-MS), Atmospheric Chemistry and Physics, 10, 10111-10128, (2010).

Analysis of organic components in secondary organic aerosols by chemical ionization mass spectrometry and discussion on mechanism of isoprene ozonolysis

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Abstract

To understand the oxidation mechanism of isoprene, we detected semi-volatile organic compounds produced in the oxidation processes of isoprene with ozone in both gaseous and aerosol phases by the same technique, e.g. proton transfer reaction – mass spectrometry (PTR-MS) and Negative Ion Chemical Ionization Mass Spectrometry (NI-CIMS). Many ion signals of the products were observed and several ion signals can be attributed to the products of the reaction of Criegee intermediates with carboxylic acid and/or aldehyde and/or ketone, which may be a key compound for the SOA formation.

Introduction

Organic material accounts for a substantial fraction of atmospheric fine particular matter that affects the global climate by direct and indirect effects as well as human health [1]. Many gas-phase organic compounds undergo oxidation in the gas phase to yield products, generally oxygenated, that have sufficiently low vapor pressures that they will partition themselves between the gas and aerosol phases. Such compounds are often referred to as semi- or non- volatile, and when residing in the aerosol phase, as secondary organic aerosols (SOA). Understanding the chemical composition and formation processes of SOA is required for a quantitative assessment of its production, properties and environmental effects [2].

Our approach for it is to detect such semi-volatile organic compounds produced in the oxidation processes in both gaseous and aerosol phases by the same technique. Proton transfer reaction – mass spectrometry (PTR-MS) is suit for such research because it allows for fast and sensitive measurements of volatile organic compounds (VOCs) at trace levels in air. In the present study, the approach was tested in the case of the oxidation of isoprene with ozone along with NI-CIMS.

Experimental Methods

SOA was produced by the reaction of isoprene with O_3 in a 6-m^3 evacuable, Teflon-coated smog chamber during 2 hours. Temporal changes of gaseous reactants and products were monitored by FTIR and PTR-MS. The size distribution of the formed SOA was measured by SMPS (scanning

mobility particle sizer) and FMPS (fast mobility particle sizer). The SOA were collected on a PTFE-filter. The sampling volume was about 0.5 m³. Then, the filter was held by a custom-built holder made of quartz. The holder was set to a sample-inlet line of the mass spectrometers and then evaporated VOCs by heating the holder from 25 °C to 80 °C step by step were detected by the mass spectrometers. Since the machine time of the smog chamber was limited, the experiments were also performed in a 1-m³ FEP bag without FTIR and FMPS. NI-CIMS data were obtained from the experiments with the 1-m³ FEP bag.

Results and Discussion

Temporal variations of reactants and products obtained by FTIR in the reaction of ozone with excess isoprene without an OH scavenger are shown in Figure 1(a). Consistent data were obtained by PTR-MS. In Figure 1(b), a temporal variation of volume concentration of SOA is shown as triangles. In the figure, the results with OH scavengers such as cyclohexane and CO are also shown. The volume concentration of SOA formed with cyclohexane was similar to that without an OH scavenger while the formation of SOA with CO was suppressed. This suggests that cyclohexane contributes to the formation of SOA and that it is not good as the OH scavenger in this reaction system. It seems that the SOA from the reaction of isoprene with ozone is obtained when CO was used as the OH scavenger.
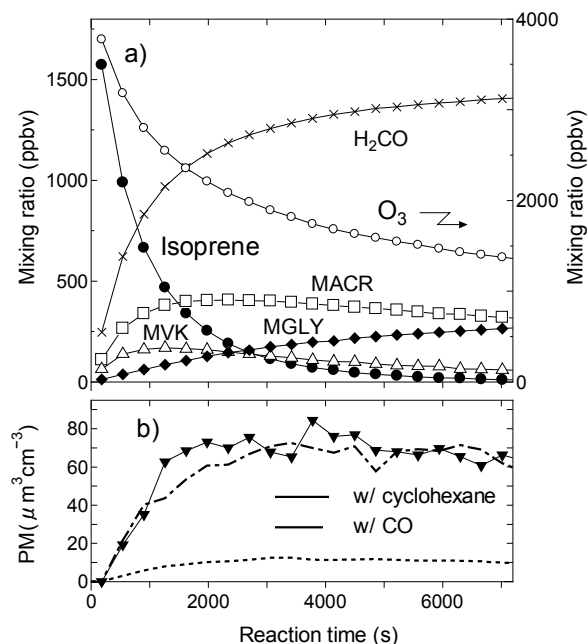
Figure 1: (a) Temporal variations of reactants (isoprene and ozone) and products (H₂CO, methacrolein (MACR), methyl vinyl ketone (MVK),and methylglyoxal (MGLY))obtained by FTIR in the reaction of ozone with excess isoprene without an OH scavenger. (b) Temporal variations of volume concentration of SOA without an OH scavenger (triangle), with cyclohexane (dash-dot line) and with CO (dot line).

Figure 2 shows PTR mass spectra obtained after 2 hours in the reaction of ozone with isoprene (a) without an OH scavenger, (b) with CO and (c) with cyclohexane. An ion signal at *m/z* 69 is assigned to isoprene and those at *m/z* 71 and 73 are attributed to the first-generation products, methacrolein /methylvinylketone, and the second-generation product, methylglyoxal, respectively. The formation of formaldehyde (*m/z* 31) and formic acid (*m/z* 47) was also observed. In addition to these major products, many ion signals up to *m/z* 150 were detected. Ion signals at *m/z* 83, 101, and 115 are decreased in the experiment with CO (Figure 2(b)) compared with the mass spectrum without OH scavenger. These ion peaks are attributed to products by the OH reaction.
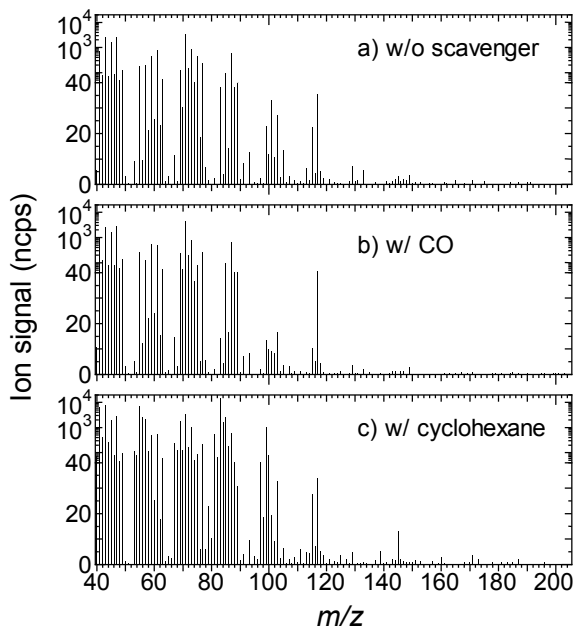
Figure2: PTR mass spectra obtained after 2 hours in the reaction of ozone with isoprene (a) without an OH scavenger, (b) with CO and (c) with cyclohexane.

Mass spectra of the SOA obtained by NIES PTR-TOFMS are shown in Figure 3. The mass spectra were summed during the heating from 25 °C to 80 °C. The observed ion signals in the SOA were similar to those observed in the gaseous phase. This suggests that chemical species that gives the ion signals exist in both gaseous and aerosol phase. In addition, the ion signals of higher mass number than *m/z* 150 were also detected in the SOA. According to the information from NI-CIMS, several ion signals observed in the PTR mass spectra can be assigned to products of the reaction of Criegee intermediates with carboxylic acid and/or aldehyde and/or ketone. These compounds may be a key compound for the SOA formation in the reaction of isoprene with ozone.

As the ion signals in the gaseous and aerosol phase were obtained by the same technique, the gas-aerosol distribution can be roughly estimated. For example, the reaction product of Criegee intermediate and methacrylic acid, whose molecular weight is 132, were observed by NI-CIMS. The ion signal of this species should be detected at *m/z* 115 by PTR-MS. From the ion signals at

m/z 115 in the gaseous and aerosol phase, the ratio of concentration in aerosol to that in gas phase was estimated to 10^{-3}. When estimating the ratios for other products from *m/z* 117 to 157, the ratios range from 10^{-4} to 10^{-2}.
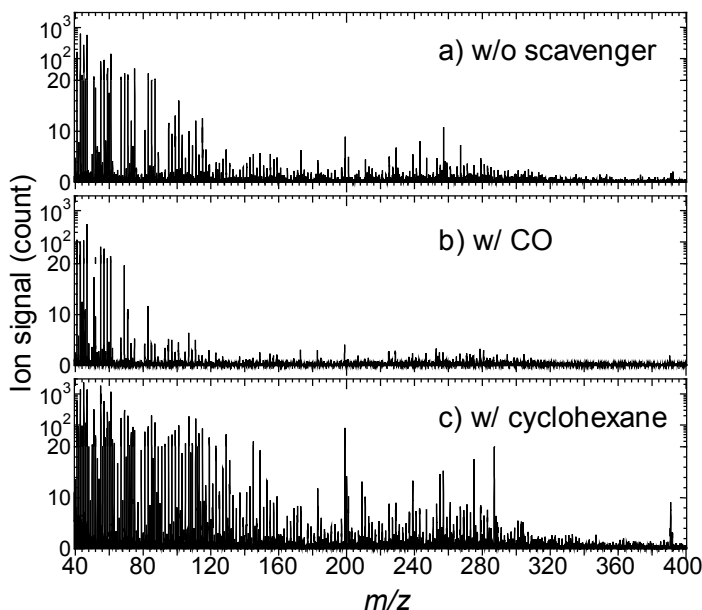
Figure 3: PTR mass spectra of evaporated VOCs from SOA formed in the reaction of ozone with isoprene (a) without an OH scavenger, (b) with CO and (c) with cyclohexane.

Acknowledgement

References

[1] M. Kanakidou, J. H. Seinfeld, S. N. Pandis, I. Barnes, F. J. Dentener, M. C. Facchini, R. Van Dingenen, B. Ervens, A. Nenes, C. J. Nielsen, E. Swietlicki, J. P. Putaud, Y. Balkanski, S. Fuzzi, J. Horth, G. K. Moortgat, R. Winterhalter, C. E. L. Myhre, K. Tsigaridis, E. Vignati, E. G. Stephanou, and J. Wilson, Organic aerosol and global climate modeling: a review, Atmospheric. Chemistry and Physics, 5, 1053-1123 (2005).

[2] S. Fuzzi, M. O. Andreae, B. J. Huebert, M. Kulmala, T. C. Bond, M. Boy, S. J. Doherty, A. Guenther, M. Kanakidou, K. Kawamura, V.-M. Kerminen, U. Lohmann, L. M. Russell, and U. Pöschl, Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, Atmospheric Chemistry and Physics, 6, 2017-2038 (2006).

Concentration and Flux measurements of Biogenic VOCs at the Oak Observatory of Haute Provence in France, spring 2012.

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Abstract

Our project (named Canopée) aims to better understand biosphere-atmosphere exchanges of biogenic hydrocarbons from Mediterranean ecosystems, and the impact of in-canopy processes on the atmospheric composition above the canopy. The measurements were carried out at the Oak Observatory of the Observatoire de Haute Provence (O3HP), situated in the southeast of France, during spring 2012. The field site is situated on a plateau, 650 meters above ground level, and presents homogeneous vegetation, with one dominant tree species: the *Quercus Pubescens* oak, a typical Mediterranean species and large emitter of isoprene. Mixing ratios and fluxes of biogenic volatile organic compounds (BVOC) were measured inside and above the canopy using online mass spectrometry (PTR-MS) and GC-FID respectively.

Introduction

The terrestrial biosphere is the main source of VOCs to the atmosphere. These compounds are present in the atmosphere at trace levels but are key components in tropospheric chemistry due to their impact on ozone formation/destruction and aerosol production. A recent study (Curci et al., 2010) estimates that BVOC emissions are responsible for the increase of tropospheric ozone levels in summer (from 5 to 15 ppb in the Mediterranean region). However, uncertainties remain concerning their emission rates from different ecosystems, and in-canopy processes involving these compounds are poorly understood. Techniques for direct VOC flux measurements have only been developed very recently, and consequently only a very limited number of ecosystem-level VOC flux measurements have taken place in the Mediterranean region (Davison et al., 2009). Therefore, there is a need for more experimental analysis in different ecosystems in order to better understand biosphere-atmosphere exchanges of VOCs and their interplay with tropospheric ozone.

Experimental Methods

The average canopy height was six meters and measurements were made at two levels, inside (2 m) and above (10 m) the canopy. Fluxes of individual VOC species were measured above the canopy using the virtual disjunct eddy covariance technique (vDEC) (Karl et al., 2002), where the flux is given as the covariance of the vertical wind speed and the gas of interest. Vertical wind speeds were measured using a sonic anemometer, fixed to a 10 m mast. The inlet line for air

sampling was next to the sonic anemometer with a high flow rate of 60 L/min in order to maintain turbulent flow and minimize signal attenuation. In order to provide both flux data and information on the full VOC composition, the PTR-MS was operating in two different modes: 50 minutes in flux mode and 10 minutes in scan mode each hour. During the flux mode, 8 protonated masses (m/z 33, 45, 59, 61, 69, 71, 87 and137) were targeted with a dwell time of 500 ms per mass. In scan mode, 5 minutes were dedicated to measure a wide range of VOCs (m/z 21-93). During the remaining 5 minutes, the PTR-MS background was monitored using an Ionimed zero air generator. PTR-MS data were stored alongside those from the sonic anemometer, using a custom logging program written in LabVIEW (National Instruments) and implemented previously by Langford et al., 2009. Two meters above the ground level, ambient concentrations of isoprene were measured at the same time exclusively by a GC-FID.

Results

Among the various VOC measured at the Oak Observatory, the most abundant was isoprene, yet concentrations of monoterpenes were very low (maximum of 200 ppt). Here we present mixing ratios and fluxes only for isoprene; profiles for other organic species will be presented at the conference. Simultaneously measured concentrations of isoprene inside and above the canopy are presented in Figure.1(a). Isoprene exhibits clear diurnal cycles. Mixing ratios increase early in the morning and rise steadily until achieving a maximum around 4:00 pm. Rapid decrease soon after sunset is observed, followed by a more gradual decline during the night. A clear gradient in concentration can be noted between the two measurement levels: maximum mixing ratios for isoprene ranged between 2-17 ppb at 2 meters a.g.l, .i.e. near the source, and between 2-7 ppb at 10 meters height, depending on environmental factors such as temperature and light. Figure.1(b) show measured isoprene fluxes relative to heat fluxes, for the period of 4-16 June. Isoprene and heat fluxes where positive during the day, with maximums ranging between 1.3-8 mg/m2/h and 260-450 W.m-2 respectively. The degradation products of isoprene, Methyl Vinyl Ketone and Methacrolein (both detected at m/z 71) are also investigated and [MVK+MACR]-to-[isoprene] ratio should give us further information about the oxidation fate of isoprene. Profiles for other organic species such as acetone, methanol, hydroxyacetone and monoterpenes will also be presented at the conference
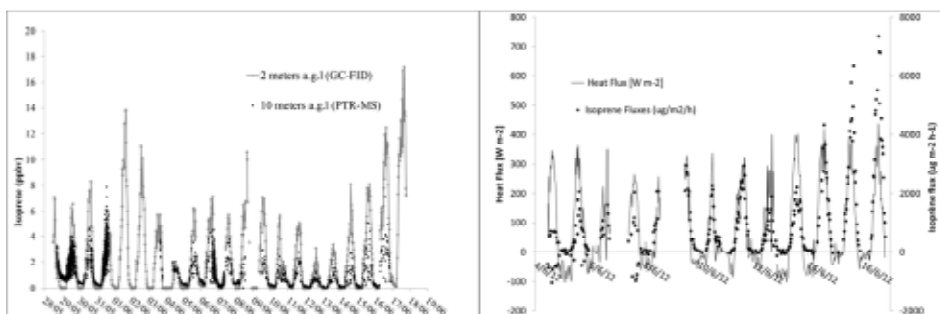
Fig.1(a) Isoprene Mixing ratios inside and above the canopy (b) Heat Fluxes and Isoprene Fluxes above the canopy.

References

[1] Curci, G., Palmer, P.I., Kurosu, T.P., Chance, K., Visconti, G., 2010. Estimating European volatile organic compound emissions using satellite observations of formaldehyde from the Ozone Monitoring Instrument. Atmos. Chem. Phys. 10, 11501–11517.

[2] Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J.N., Rinne, J., Hewitt, C.N., 2009. Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy. Biogeosciences 6, 1655–1670.

[3] Karl, T.G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall, R., Guenther, A., 2002. Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry. Atmospheric Chemistry and Physics 2, 279–291.

[4] Langford, B., Davison, B., Nemitz, E., Hewitt, C.N., 2009. Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK). Atmos. Chem. Phys. 9, 1971–1987.

PTR-MS application for biofiltration kinetics assessment of odour removal

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Abstract

The PTR-MS was applied to measure the odour decayed profile in a bag incubation experiment. The purpose was to estimate the kinetics parameters of biodegradation of the odour. Hydrogen sulfide was chosen as a typical odour due to its offensive feature, relatively high concentration in the ventilation air emitted from intensive pig facilities and low removal efficiency compared to some other odours (e.g., carboxylic acids, phenols, etc.). The kinetics assessment of the hydrogen sulfide removal in the bag incubation experiment was preceded through the established kinetis model using the measured decayed profile by the PTR-MS. The results showed that the maximum biodegradation rate of hydrogen sulfide in the 3rd stage of the biofilter is much higher than that in the first two stages, which could be explained by the more presented fungi in the 3rd stage of the biofilter.

Introduction

Odour emitted from intensive pig production may cause severe nuisance to neighbours and therefore need to be reduced. Biofiltration has emerged as a cost-effective technology for odour removal from ventilation air emitted from intensive pig facilities [1-5]. However, volatile sulfur compounds showed low removal efficiencies in biofilters and this may due to the poor water-solubility, the low mass transfer process or the low biodegradation. Since hydrogen sulfide is an offensive odour with a low odour threshold and relatively high concentration in the ventilation air, it is certainly a need to investigate the removal kinetics of hydrogen sulfide in order to improve the performance of the biofilter.

This study applied PTR-MS to measure the decayed profile of hydrogen sulfide in a bag incubation experiment and thereafter the data was used for estimation of the kinetics parameters of the removal of hydrogen sulfide. The purpose was to see if these kinetic assessments could be applied into a micro-model simulating the dynamic biofiltration process.

Experimental Methods

Three-stage biofilter

A full-scale three-stage biological air filter was installed next to a pig production facility in Denmark. The packing material used in the biofilter was made of cellulose pads (with specific surface area $383 \ m^2 \ m^{-3}$, [6]). The first 2 stages had a depth of 0.15 m for each and were irrigated with recirculated water regularly. The 3rd stage had a depth of 0.6 m and was supplied with humidified air from the first 2 stages without irrigation [7].

Bag incubation experiments

A few biofilter cores were taken from the running three-stage biofilter for the bag incubation experiments. Two pieces of cores were taken from the first 2 stages (with diameter of 4 cm and 15 cm for length) and three pieces were taken from the 3rd stage filter (from 0-20 cm, 20-40 cm and 40-60 cm, respectively; diameter of 10 cm and 20 cm for length). Each core was put into a 10 L Tedlar bag filled with zero-air. The H_2S were injected into the Tedlar bag with a designed initial H_2S concentration. The decay of H_2S in the bag was measured by PTR-MS after dilution in order to keep the low flow out of the bag and thus the loss of air from the bag was negligible.

PTR-MS

A high-sensitivity PTR-MS was applied for the experiments. The PTR-MS was operated under standard ion drift tube conditions. Total voltage was set to 600v, the drift tube temperature was set to 60 degree and the pressure in the drift tube was around 2.18. The E/N number was controlled ca. 135 Td. The humidity dependence of H_2S was calibrated before and after the experiments [8].
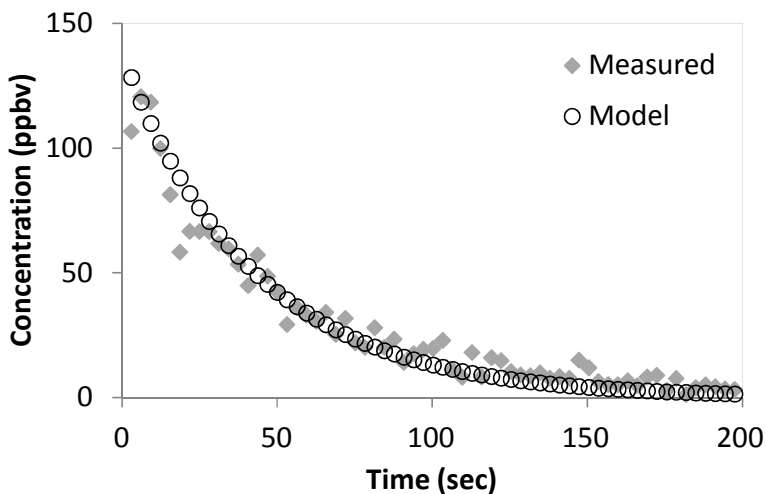
Figure 1: An example of the measured decay profile and simulated decay profile by the established model.

Kinetics assessment

The kinetics of the biodegradation of hydrogen sulfide was estimated by an established kinetics model. The model assumed that the gas was uptaken by the biofilm with first-order kinetics rate of k_1, and with back diffusion through kinetics rate of k_{-1}. The biodegradation rate was assumed to follow Michaelis-Menten kinetics [9]. Thus the kinetics could be decribed as below:

$$\text{HSH(g)} \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \text{HSH(b)} \quad \overset{k_{max}, K_i}{\rightarrow} \quad \text{Product}$$

(1)
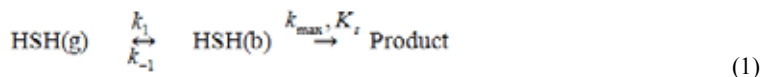
The biofilm thickness for the first 2 stages was assumed to be ca. 200 μm, and 20 μm for the 3rd stage of the biofilter.

Results and Discussion

The results showed that the measured decayed profile of hydrogen sulfide could be simulated by the established model which could estimate the kinetics parameters for the removal of hydrogen sulfide in the three stage biological air filter. One example is shown in Figure 1 describing the fitting of simulated data to the measured data for the 3rd stage of the biofilter (0-20 cm). The results indicated the uptaken rates (k_1) of hydrogen sulfide in all 3 stages were comparable to the overall mass transfer rate measured for cellulose pads by Liu et al. (10). Whereas the maximum removal rate (k_{max}) for the hydrogen sulfide in the first two stages were comparable to the last part of the 3rd stage of the biofilter (40-60 cm), the maximum removal rate in the first part of the 3rd stage of the biofilter is around 10 times higher, which was observed as more dense fungi presented in the field measurements in the previous study [5, 11].

References

[1] D.H. O'Neill, I.W. Stewart, V.R. Phillips, A review of the control of odour nuisance from livestock building: Part 2. The cost of odour abatement systems as predicted from ventilation requirements, Journal of Agricultural Engineering Research 51, 157–165, (1992).

[2] R.E. Nicolai, K.A. Janni, Biofilter media mixture ratio of wood chips and compost treating swine odors. Water Science & Technology 44, 261–267, (2001).

[3] R.W. Melse, N.W.M. Ogink, Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands. Transactions of the ASAE 48, 2303-2313, (2005).

[4] L. Chen, S. Hoff, L. Cai, J. Koziel, B. Zelle, Evaluation of wood chip-based biofilters to reduce odor, hydrogen sulfide, and ammonia from swine barn ventilation air. Journal of Air & Waste Management Association 59, 520−530, (2009).

[5] M. J. Hansen, D. Liu, L. B. Guldberg, A. Feilberg, Application of Proton-Transfer-Reaction Mass Spectrometry to the assessment of odorant removal in a biological air cleaner for pig production. Journal of Agriculture and Food Chemistry 60, 2599−2606, (2012).

[6] L.D.M. Ottosen, S. Juhler, L. B. Guldberg, A. Feilberg, N. P. Revsbech, L. P. Nielsen, Regulation of ammonia oxidation in biotrickling airfilters with high ammonium load, Chemical Engineering Journal 167, 198−205, (2011).

[7] D. Liu, M.J. Hansen, L.B. Guldberg, A. Feilberg, Kinetic evaluation of removal of odor contaminants in a three-stage biological air filter, Environmental Science & Technology 46, 8261-8269, (2012).

[8] A. Feilberg, D. Liu, A.P.S. Adamsen, M.J. Hansen, K. Jonassen, Odorant emissions from intensive pig production measured by online proton-transfer-reaction mass spectrometry, Environmental Science & Technology 44, 5894-5900, (2010).

[9] M. Hirai, M. Ohtake, M. Shoda, Removal kinetics of hydrogen sulfide, methanethiol and dimethyl sulfide by peat biofilters, Journal of Fermentation and Bioengineering 70, 334-339, (1990).

[10] D. Liu, A.P.S Adamsen, R.R. Andreasen, T.G. Poulsen, A. Feilberg, A comparative study of mass transfer coefficients of reduced volatile sulfur compounds regarding packing materials for biofiltration. To be submitted, (2013).

[11] C.L. Pedersen, D. Liu, M.J. Hansen, A. Feilberg, L.H. Søgaard, L.B. Guldberg, A. Schramm, L.P. Nielsen, Sulfide oxidation in a biofilter. Poster in 14th International Symposium on Microbial Ecology, Copenhagen, Denmark, 19-24 August, (2012).

PTR-MS measurements of eddy covariance fluxes and concentrations of VOCs from aircraft over California

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Abstract

An aircraft flux study was conducted to assess BVOC emissions from California ecosystems with a focus on oak woodlands. The direct eddy covariance (vDEC approach) approach used a PTR-MS onboard a CIRPAS Twin Otter aircraft during June 2011 as part of the CABERNET (California Airborne BVOC Emission Research in Natural Ecosystem Transects) project. The results as well as the technicalities of PTR-MS operation on the aircraft are discussed here. This has been the most precise determination of direct fluxes and emission factors of BVOC from aircraft transects over vegetative areas and "race-track" profiles over homogenous and nonhomogeneous oak landscapes allowing accurate measurements at high spatial resolution (less than 2 km).

Introduction

Oaks belong to the highest isoprene emitting broadleaf tree species, and they grow in specific elevations which makes them an ideal exploratory subject to study from an aircraft. In California the majority of oak woodlands surround the polluted Central Valley. MEGAN [1] and BEIGIS [2] models are commonly used to predict emissions of BVOCs in California. Since the distribution of oaks is relatively sparse, their LAI is not as high as that of densely forested regions in the Sierra Nevada Mountains which are dominated by conifers emitting mainly methanol, methylbutenol, and terpenes but only very little of isoprene. The oak woodlands can therefore be regarded as a specific case for regional modeling. PTR-MS has been increasingly used on aircraft for measurement of concentrations [3] and recently also for the direct fluxes [4]. The flux quality depends on the optimal aircraft characteristics (e.g., low speeds, turbulence probe of high precision, etc.) but equally important is the instrument optimization to ensure high absolute sensitivities, short response times, and stable operation during the flights. The sampling inlet is typically adjusted for pressure control in a wider range in order to ensure stable drift-tube conditions at low atmospheric pressures. The signal from a turbulence probe requires calibration which can be performed in so called Lenschow maneuvers [5] to obtain coefficients for transformation of vertical wind speeds to be independent of the aircraft motion. For low altitude flights airborne flux footprint can be in the order of just a few km. This offers a great advantage over the measurements of just the concentrations in particular in terms of the compounds with long atmospheric lifetimes such as methanol which can be advected hundreds of km away from the source over long temporal scales. Here, these direct flux measurements are shown to improve biogenic emission model predictions whose accuracy was found to depend mostly on the accuracy

of the input datasets (emission factors, landcovers, micrometeorology, etc.) rather than on the framework of these models. The eddy-covariance technique also proved to work well for geolocation of the VOC sources and sinks.

Experimental Methods

Instrument preparation

A high sensitivity PTR-MS instrument was optimized for aircraft deployment. The sampling inlet of the vacuum system was adjusted to allow for stable operation in a broader span of atmospheric pressures. In addition, the automatic back-flushing system was installed to sample pure air with low concentration isoprene standard to avoid potential inlet contamination during the take-offs/landings and to cross-check isoprene sensitivity with daily calibrations for selected VOCs. The instrument preparation was also focused on complying with the new stricter regulations such as the 18-g requirement for the instrument rack.

Aircraft

A twin otter aircraft was requested from CIRPAS (The Center for Interdisciplinary Remotely-Piloted Aircraft Sudies). This aircraft offers many advantages for eddy covariance studies which include: 1) high-flow isokinetic inlet; 2) 5-hole turbulence probe delivering 10 Hz 3D wind speed data; 3) decent payload capacity (700 kg); 4) ability to fly relatively slowly (~ 50 m/s), steadily and evenly; 5) approx. 1000 km range fully loaded; 6) intercom ground communication; and 7) an experienced team of pilots and engineers. The data acquisition used a PTR-MS Control LabVIEW software (version 7 build 155) and a customized LabVIEW software using the API functions to combine the meteorological aircraft-sensors and PTR-MS data for an online preview of selected parameters versus altitude, estimation of PBL heights and the altitudes for profile levels. Some of the online concentration data were being exported via the intercom system to the ground teams for live observation of the data and flight tracks.

Flights

Nearly 10,000 km were covered with 100% instrument uptime. Oak woodlands were the primary target for this biogenic VOC flux study. Figure 1 shows the flown flight tracks overlayed on the oak distribution from the GAP landacover. We have covered most of these terrains and performed "race track" profiles in homogenous and non-homogenous oak woodland areas.

Figure 1: CIRPAS aircraft and flight tracks covering most of oak woodlands.

Airborne eddy covariance

The scalar conservation equation of an atmospheric tracer can be given as

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + \frac{\partial F}{\partial z} = S$$

(1)

where C denotes the concentration, U is the mean speed and S represents the sink and source term. F is the turbulent flux, which can be expressed as a covariance between the instantaneous deviation in concentration and instantaneous deviation in vertical wind speed (F= cov(c'w')). The second and third term of the equation 1 correspond to advection and flux divergence, respectively. The latter term can be determined from the vertical profiles over a homogenous source terrain providing the coeffcients for scaling the flux at the aircraft altitude to the flux at the surface. Flux can be derived using two independent methods: 1) Fast Fourier Transform (FFT) which delivers a single value of the flux integrated over an aircraft leg; and 2) Continuous Wavelet Transformation (CWT) [6] which not only can reconstruct the frequency but also the time domain, providing an "instantaneous" flux over chosen bandwidth. Thus, this method is not affected by non-stationarities and its average for the flight leg can be independently compared to the FFT flux serving an additional quality control.

Comparison of fluxes to MEGAN and BEIGIS model outputs

The surface flux derived from wavelet approach was averaged to 2 km resolution to allow for direct comparison with the model predictions. For the emission factor comparison the flux data were normalized for surface temperature and downward PAR by deviding the surface flux by the activity factor of the Guenther et al. 2006 [8] algorithm. These emission factors were subsequently compared with emission factors used in MEGAN and BEIGIS.

Results

In the flux processing of the transects relatively long and straight segments (from approx. 50 to 300 km) were integrated, and uneven segments such as turns, climbs (e.g. soundings) or decents were rejected. The peak in the covariance function was very clear and the quality of the co-spectra independently determined by the FFT and wavelet methods was very high with the FFT to wavelet flux ratios typically ranging from 0.9 to 1.3. Figure 2 presents isoprene concentrations, and isoprene measured emission factors overlayed over emission factors used in MEGAN 2.1[1] showing. Isoprene flux over oaks was very high (exceeding 4 mg m^{-2} h^{-1}), but was small over all other landscapes. Isoprene emissions from agricultural crop regions and shrublands were generally low, but high methanol and monoterpenes were found above some of these regions.
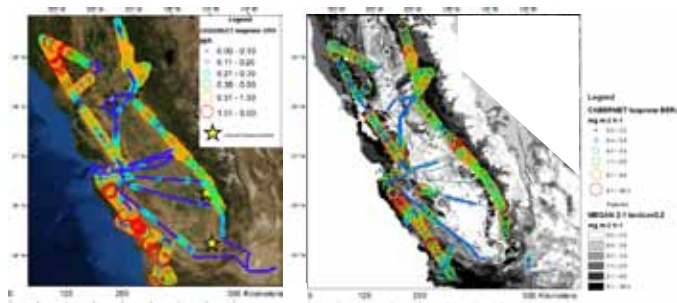
Figure 2: Isoprene volume mixing ratios over satellite imagery (left) and measured emission factors overlayed on emission factors obtained from MEGAN 2.1 landcover (right)

Discussion

Accurate species composition and aircraft-derived emission factors are critical for the improvement of the accuracy of modeled predictions for isoprene and other important ozone and aerosol precursor compounds. We succeeded in measuring emissions with the largest coverage with respect to biogenic sources, so far conducted, of isoprene, MVK+MAC, methanol, monoterpenes, and MBO. Eddy covariance technique from aircraft offered extremely high accuracy and seems appropriate for regional studies of VOC emissions. Although isoprene mixing ratios and fluxes showed similar spatial patterns, methanol, whose atmospheric life time is much longer, showed different patterns of concentrations and fluxes. Methanol eddy covariance fluxes obtained from aircraft during CABERNET could easily identify major sources such as dairies, and major sinks such as vegetative areas downwind dairies. This points to the fact that concentrations alone may not tell the whole story and could be elevated even in the areas far away from their sources. This has been the most precise determination of direct fluxes and emission factors of BVOCs from aircraft.

Acknowledgements

References

[1] Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev. Discuss., 5, 1503-1560, doi:10.5194/gmdd-5-1503-2012, 2012.

[2] Scott, K. I., & Benjamin, M. T. (2003). Development of a biogenic volatile organic compounds emission inventory for the SCOS97-NARSTO domain. Atmospheric environment, 37, 39-49.

[3] Warneke, C., De Gouw, J. A., Del Negro, L., Brioude, J., McKeen, S., Stark, H., ... & Hanks, A. C. (2010). Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with biogenic emission inventories. Journal of Geophysical Research, 115(D7), D00F18.

[4] Karl, T., Apel, E., Hodzic, A., Riemer, D. D., Blake, D. R., & Wiedinmyer, C. (2009). Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity. Atmos. Chem. Phys, 9(1), 271-285.

[5] Lenschow, D. H. (1986). Probing the atmospheric boundary layer. Amer Meteorological Society.

[6] Mauder, M., Desjardins, R. L., and MacPherson, I.: Scale analysis of airborne flux measurements over heterogeneous terrain in a boreal ecosystem, J. Geophys. Res., 112, D13112, doi:10.1029/2006JD008133, 2007.

Total OH reactivity fluxes from Norway spruce

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Abstract

Numerous reactive volatile organic compounds (VOCs) are emitted into the atmosphere by vegetation. Most biogenic VOCs are highly reactive towards the atmosphere's most important oxidant, the hydroxyl radical (OH). One way to investigate the chemical interplay between biosphere and atmosphere is through the measurement of total OH reactivity, the total loss rate of OH radicals.

This study presents the first determination of total OH reactivity emission rates based on a branch cuvette mounted on a Norway spruce (Picea abies) throughout spring, summer and autumn 2011. The total OH reactivity was measured inside the branch enclosure using the Comparative Reactivity Method (CRM) with a Proton Transfer Reaction-Mass Spectrometer (PTR-MS) as detector. In parallel, separate VOC emission rates were monitored by a second PTR-MS, including the signal of isoprene, acetaldehyde, total monoterpenes and total sesquiterpenes.

Total OH reactivity emission rates were in general temperature and light dependent, showing strong diel cycles with highest values during daytime. Monoterpene emissions contributed most, accounting for 56-69 % of the measured total OH reactivity flux in spring and early summer. However, during late summer and autumn the monoterpene contribution decreased to 11-16 %. At this time, a large missing fraction of the total OH reactivity emission rate (70-84 %) was found when compared to the VOC budget measured by PTR-MS. Total OH reactivity and missing total OH reactivity emission rates reached maximum values in late summer corresponding to the period of highest temperature.

During these times, unmeasured and possibly unknown primary biogenic emissions contributed significantly to the observed total OH reactivity flux.

Real-time analysis of sulfur-containing volatiles in *Brassica* plants infested with root-feeding *Delia radicum* larvae using proton-transfer reaction mass spectrometry

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Abstract

Plants damaged by herbivores emit a variety of volatile organic compounds (VOCs). Here we used proton-transfer reaction mass spectrometry (PTR-MS) as a sensitive detection method for online analysis of herbivore-induced VOCs. Previously, it was found that *Brassica nigra* plants emit several sulfur-containing VOCs when attacked by cabbage root fly (*Delia radicum*) larvae with m/z 60 as a marker for the formation of allylisothiocyanate from the glucosinolate sinigrin. We tested the hypothesis that m/z 60 emission occurs only in plants with sinigrin in their roots. Additionally, we tested the hypothesis that methanethiol, dimethylsulfide and dimethyldisulfide are only emitted after larval infestation.

Proton-transfer reaction mass spectrometry was used to track sulfur-containing VOCs from six different species of *Brassica* over time. The roots were either artificially damaged or infested with cabbage root fly larvae. Glucosinolate profiles of the roots were analysed using high pressure liquid chromatography and compared with VOC emissions.

Results

Artificial wounding with a scalpel as well as damage with D. radicum larvae resulted in two types of primary response among the six plant species. Three out of six Brassica plant species, namely B. nigra, B. juncea and B. napus, primarily emitted m/z 60 and the three other species, B. rapa, B. carinata and B. oleracea, emitted methanethiol as the primary compound immediately after artificial root damage (Figure.1). Even though methanethiol was the primary compound emitted after root damage, m/z 60 emissions were also enhanced in artificially damaged B. oleracea and B.carinata.

Glucosinolate profiles and concentrations in the roots were similar to those reported for mature roots of B. nigra, B. juncea, B. rapa and B. napus [1]. Among the six species of Brassica under study, B. nigra, B. juncea, B. oleracea and B. carinata showed the presence of sinigrin in their roots, whereas B. napus and B. rapa did not contain sinigrin (Figure.2).

The root glucosinolate profiles of these six Brassica species were compared with VOC emissions as measured in the PTR-MS to test the hypothesis that the conversion of sinigrin is required for the emission of m/z 60. Apparently, this was not the case, as B. napus roots, which lack sinigrin, clearly emitted m/z 60 after artificial damage. On the other hand, the emissions of m/z 60 in B.

carinata were relatively low despite the fact that these roots had the highest sinigrin levels of all species.

Discussion:

The primary compound that was emitted by each species was consistent for artificial and natural root damage. The type of sulfur-containing compounds that were emitted after damage thus depends mainly on plant species and not on the type of damage that is inflicted. Our results also challenge the hypothesis that the presence of sinigrin is the main factor for m/z 60 emissions; plants lacking sinigrin in their roots also showed enhanced emissions of m/z 60 after damage.

Previously, it was established experimentally that the emission of m/z 60 as an immediate response after artificial damage to *B. nigra* was related to the glucosinolate– myrosinase system that is constitutively present in Brassica plants [3]. Most notably, allylITC, the product formed after the reaction of sinigrin with myrosinase, was found to yield m/z 60. 2-PhenylethylITC, the product of the reaction of myrosinase with gluconasturtiin—the other main root compound in *B. nigra*—did not result in m/z 60. However, our current study shows that there may be other sources for the m/z 60 signal than sinigrin alone. This hypothesis, however, now needs testing by analysing the various ITC that may arise from the reactions of these glucosinolates with myrosinase in the PTR-MS.

Other than the production of ITC and related products from glucosinolates, the emission of methanethiol and sulfides is not exclusively linked to members of the *Brassicaceae*. However, in *Brassica* species there is also a more specific plant-based source of sulfides that is related to the formation of glucosinolate conversion products. High levels of thiol methyltransferase (TMT) activities have been found in shoots and roots of various *Brassica* species [2]. This enzyme is thought to have a function in detoxifying the phytotoxic sulfur-containing (by) products of glucosinolate conversion, such as cyanides and HS2 ions. Thiol methyltransferase methylates ITC and related sulfur-containing reaction products from glucosinolate conversions, thereby producing methylsulfides [2].

This suggests that the level of TMT activity may play an important role in the production of sulfides versus ITC and co-determines which sulphur compound is primarily formed after artificial and natural root damage. Based on their emission patterns, it can be hypothesized that *B. carinata* should have TMT activity levels close to those of *B. oleracea*, whereas *B. nigra* TMT activities would be close to those of *B. juncea*. Further analyses of TMT activities in these species, especially in the roots, should be performed to confirm this hypothesis.

It was found that the midgut of *D. radicum* larvae contains a wide range of (symbiotic) bacteria which are essential to digest the tough root tissue that the larvae feed on. The bacterial gut community included several Serratia species, some of which emit DMDS, DMTS and methanethiol when grown on artificial medium. The slower evolving emissions of methanethiol in *D. radicum*-infested *B. nigra* and *B. juncea*—which did not occur in artificially damaged plants of these species—may therefore come from the growing population of gut bacteria in the digested root materials. However, the immediate emission of methanethiol after artificial damage in *B. rapa, B. oleracea* and *B. carinata* suggests that exposure to gut bacteria is not an absolute requisite for the production of these volatiles. Further research is needed to determine the relative roles of plant enzymes such as TMT and bacterial gut communities in the formation of these volatile compounds.
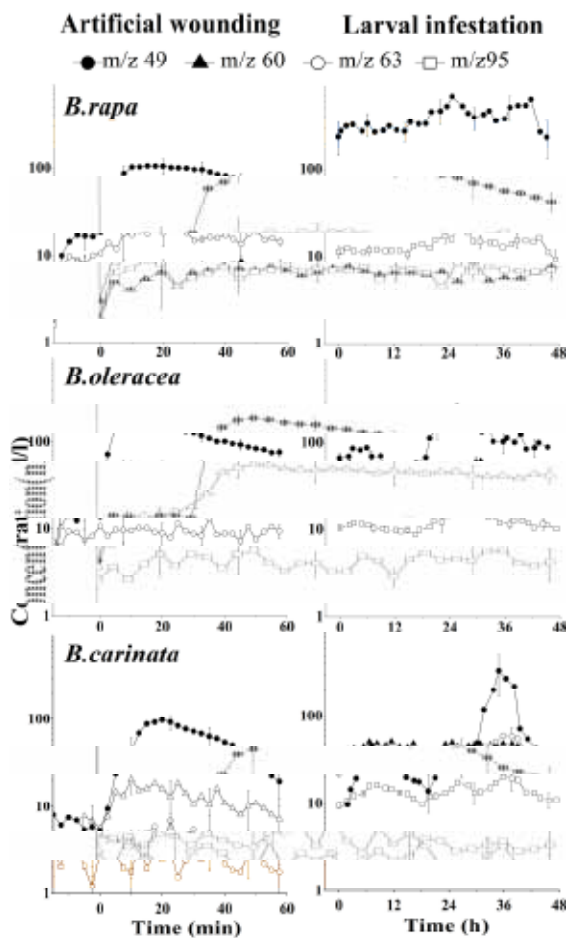
Figure 1: Emission of sulfur-containing volatile compounds after root damage by artificial wounding with a scalpel (left panels) or larval infestation (right panels) in B. rapa (A, B), B. oleracea (C, D) and B. carinata (E,F). m/z 60—ITC marker, m/z 49—methanethiol, m/z 63— DMS and m/z 95—DMDS. Vertical bars indicate the standard error of the mean (n ¼ 3). In (A), (C) and (E), t ¼ 0 indicates the time at which the root was damaged with a scalpel. In (B), (D) and (F), t ¼ 0 is the starting time of PTR-MS analysis; Delia larvae were added to plants 2–3 h before analysis.
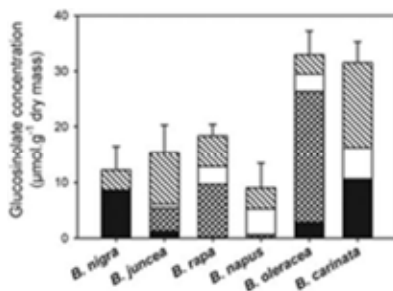
Figure 2: Glucosinolate concentrations and profiles in roots of six different Brassica species. Error bars indicate standard error of the mean of the total glucosinolate concentration (n ¼ 5– 7 per species). Black bars: sinigrin (allyl glucosinolate); crossed bars: aliphatic glucosinolates other than sinigrin; white bars: indole glucosinolates; striped bars: 2-phenylethylglucosinolate.

Conclusions:

The principal compound emitted after root damage is determined by the plant species, and not by damage type or root glucosinolate composition. Once determined, the principal compounds may be used as markers for identifying damaged or infested plants. Further analyses of plant enzymes involved in the breakdown of sulfur compounds is needed to reveal the origin of sulfur-containing VOCs from plants.

References

[1] Bellostas N, Sorensen JC, Sorensen H. 2007. Profiling glucosinolates in vegetative and reproductive tissues of four Brassica species of the U-triangle for their biofumigation potential. Journal of the Science of Food and Agriculture 87: 1586–1594.

[2] Attieh J, Kleppinger-Sparace KF, Nunes C, Sparace SA, Saini HS. 2000. Evidence implicatinga novel thiol methyltransferase in the detoxification of glucosinolate hydrolysis products in Brassica oleracea L. Plant, Cell and Environment 23: 165–174.

[3] Crespo E, Hordijk CA, De Graaf R, Devasena Samudrala, Cristescu SM, Harren FJM, van Dam NM. 2012. On-line detection of root-induced volatiles in Brassica nigra plants infested by Delia radicum L. root fly larvae. Phytochemistry, 84:68-77.

Combined Gas/Particle Source Apportionment in a European Megacity

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Abstract

Gaseous and particulate atmospheric organic compounds are emitted from a highly complex set of sources. The composition of these emissions is further affected by gas/particle partitioning and atmospheric reactions. Recent studies have highlighted the complex interrelationships between the gas and particle phases, demonstrating the need for analytical approaches capable of treating these two phases simultaneously. Here we present positive matrix factorization analysis of combined gas and particle phase measurements by proton transfer reaction mass spectrometry (PTR-MS) and aerosol mass spectrometry (AMS) for summer and winter intensive measurement campaigns in the European megacity of Paris. Identified sources included traffic, biomass burning, cooking, and several factors relating to secondary reaction products which could be separated by geographic origin (marine vs. terrestrial), production (day vs. night), and extent of oxygenation (relating to atmospheric age and/or lifetime). Inclusion of the gas-phase measurements enabled deconvolution of particle factors that were mixed in AMS-only factor analysis; likewise inclusion of the particle data helped clarify the PTR-MS factors. The joint analysis provides a comprehensive description of the sources and processes affecting Paris air quality.

PTRMS onboard passenger and research aircraft: technical realization, performance, and results

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Abstract

Within the framework of the CARIBIC project a modified PTRMS from Ionicon is deployed in the cargo bay of a Lufthansa passenger aircraft (A340-600) with a frequency of ~40 flights per year since 2006. In addition, a home-made light-weight PTRMS has been developed for the use onboard the new German research aircraft HALO (High-Altitude and LOng-range aircraft, Gulfstream GV-550), with the first chemical mission in summer 2013 (OMO-EU). This instrument was tested on ground (stationary and installed in a driving van) during the UBWOS campaign in January to March 2012 in Utah, USA, see contributions by Geiger et al. and by Warneke/Graus. We shortly describe the features of the two devices and the experiences made. Some scientific results are discussed such as the seasonal and vertical variation of acetone in the upper troposphere / lower stratosphere (UTLS), the yield of OH radicals due to the photolysis of acetone, and the detection of extreme VOC levels in the ppmv-range during UBWOS.

Introduction

CARIBIC (www.caribic-atmospheric.com) operates since 1997, first onboard a Boeing-767 of LTU airlines (1997-2002) and since 2005 onboard a Lufthansa Airbus. The specifically modified aircraft is equipped on a monthly basis with an airfreight container (1.6 tons) that currently houses 15 instruments, for 2-4 long distance flights from Germany to destinations worldwide. A strongly modified PTRMS was installed in December 2004 and measures, with a two year break 2009-2010, acetone, acetonitrile, acetaldehyde and methanol. It is the sole in-situ device worldwide that regularly monitors VOCs in the UTLS with high spatial resolution.

Because of weight and size limitations onboard research aircraft, we decided to develop a lightweight quadrupole PTRMS that should show at least the sensitivity of the original PTRMS. The total weight including zero-air generator and calibration system is below 50 kg (without aircraft rack) and currently shows the identical performance as the CARIBIC PTRMS. The instrument is completely automated and controls all instrument components depending on altitude (pressure) and flight phase. It is equipped with EMI filters, mechanical shock absorbers for sensible parts and contains negligible amounts of flammable materials. The aircraft-certification will be finished until April 2013. The first airborne deployment is envisaged for the campaign "Oxidation Mechanism Observations (OMO) - EU" in July/August 2013.

Experimental Methods

The CARIBIC PTRMS is a modified version of a commercial IONICON instrument. The complete electrical power concept was changed to the aircraft power of 28 VDC. The instrument control now relies on LabView-based software that allows unattended running of all instrument components, dependent on the actual flight phase and for some subsequent flights. The instrument weight was decreased by ~25 kg, inter alia by exchanging the large and bulky high-vacuum turbo

pump by a light-weight pump (because of which the sample air throughput had to be decreased by ~40%).

The HALO PTRMS is a completely custom-made instrument. It houses three (small) turbo pumps, the entire tube/flange system is made of stiff aluminum alloy and the entire housekeeping and electronics, including the high-voltage supplies for the ion source, drift tube, and quadrupole detection system, as well as the counting and mass selection, is integrated in one electronic module of ~4 kg weight. The calibration is done based on an unheated permeation system filled with isotopically labeled VOCs [2].

CARIBIC observations

As an example, Fig. 1 indicates the mean distribution of acetone relative to the tropopause (typical altitude: 10-11 km) in the mid-latitudes (38° – 60°N) over the year. There is a strong seasonal variation in the upper troposphere, with mean concentration of ~300 pptv in winter and ~900 pptv in summer, which reflects the stronger convective uplift of polluted acetone-rich air in summer, but also the stronger in-situ production in the troposphere generated by the chemical degradation of small alkanes and isoalkanes (first of all propane) and other precursor species (e.g. terpenes). The subsidence of clean, acetone-poor stratospheric air masses in spring with mixing ratios of below 50 pptv is clearly visible [1].
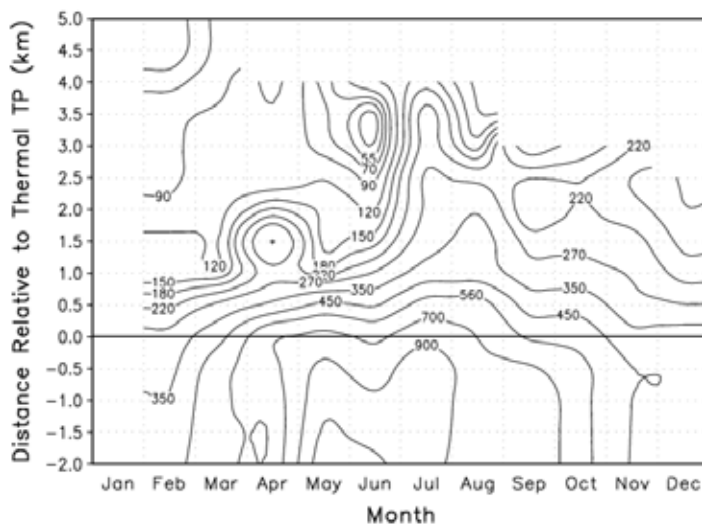
Figure 1: Seasonal variation of acetone (in pptv) for a range of distances relative to the thermal tropopause. Data from February 2006 to December 2008.

The importance of acetone in the atmosphere is particularly based on its role as precursor of OH, the dominant detergent in the atmosphere. The combination of the CARIBIC data of acetone, ozone (O_3) and water vapor (H_2O) with the (time and altitude dependent) photolysis frequencies for acetone and ozone retrieved by the global chemistry and climate model EMAC let to the conclusion that the OH production rate from acetone photolysis amounts to 1/3 to 2/3 of the one from the photolysis of O_3 and subsequent reaction of $O(^1D)$ with H_2O.

Deployment of HALO instrument

Because of substantial delay of the HALO certification process, the HALO device was first used during the Uintah Basin Winter Ozone Study (UBWOS) campaign in Utah, Colorado, US, between January and March 2013, in very close collaboration with NOAA (Carsten Warneke, Martin Graus, Joost de Gouw), see contributions by Geiger et al. and by Warneke/Graus. Scientific goal was the better understanding of the strongly elevated concentrations of ozone (and precursor substances) over the (usually) snow-covered region in the Uintah Basin where about 5000 oil and gas production sites are located, widely using the fracking technique associated with the use of complex chemical cocktails pressed into the wellheads.

The HALO instruments was used both stationary and in an instrumented van that drove near and between the different production sites. Total mass scans between 20 and 170 amu showed partially extremely elevated levels of diverse aromatics of up to 10 ppmv close to the flow back site Glen Bench.

Future

Both instruments will be further modified and improved in order to enhance their sensitivity and number of detected species. The very dry air masses in the UTLS typically showing H_2O mixing ratios between 5 and 200 ppmv and thus weak H_2O clustering in the drift tube will help to measure reactive species such as formaldehyde (CH_2O) or peroxyacyl nitrate (PAN).

The datasets of CARIBIC and HALO will be combined to deliver representative long-term datasets of diverse VOCs in the UTLS, but also profile information from the boundary layer up to the stratosphere under multifaceted meteorological and geographical situations. Goal is a better understanding of the budget (sources, sinks, chemical processing) of VOCs in the free atmosphere.

References

[1] Sprung, D., and Zahn, A., Acetone in the upper troposphere/lowermost stratosphere measured by the CARIBIC passenger aicraft: Distribution, seasonal cycle, and variability, J. Geophys. Res. 115, D16301, doi:10.1029/2009JD012099, 2010.

[2] Brito, J. and A. Zahn, An unheated permeation device for calibrating atmospheric VOC measurements, Atmos. Meas. Tech., 4, 2143-2152, doi:10.5194/amt-4-2143-2011, 2011.

Contributed Papers (Posters)

Breath analysis on animal models and humans as a non invasive tool for studying liver diseases and their interaction with diet.

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Abstract

The upgrade of PTR-MS from Quadrupole to Time of Flight mass spectrometer [1] represents a great advance in the analytical capability of PTR-MS technology. Due to higher mass range and higher mass and time resolution [2-3], ToF mass analyzers appears to be an ideal tool for breath monitoring. On the other hand the larger and more complex data generated requires great efforts to handle and extract the analytical information. We recently developed a full methodology from basic mass spectra handling to the application of up-to date data mining methods [4] which allows for extracting highly relevant features from large amounts of complex spectral data.

Here we present our recent experiences in breath monitoring using PTR-ToF-MS for non-invasive physiology monitoring and disease diagnosis. The first application is the monitoring of the effects of the diet on the physiology state in awake rats affected by non-alcoholic steatohepatitis (NASH) [5]. The second application is the implementation of a procedure for the diagnosis of liver cirrhosis and the assessment of disease severity in humans.

Application 1.

Rat suffering of NASH were subjected to 2 different diet regimes (standard or high fat). Since in a recent study was demonstrated that decaffeinated coffee reduces liver inflammation [6], water or decaffeinated coffee was administrated to the rats to verify if through breath analysis was possible to see also such effect. In the rats' exhaled breath we found several spectrometric peaks that are reliable markers both for diet fat content or coffee supplementation. The high resolution and accuracy of PTR-ToF-MS allows the identification of related compounds such as methanol, dimethyl sulphide, dimethyl sulphone and ammonia most of them related to the metabolism of liver inflammation.

In conclusion the rapid and minimally invasive breath analysis of awake rats allows the identification of markers related to the pathologic conditions and the influence of the diet on it.

The use of animal models for disease studies has the advantage to reduce the confounding factors induced by non standardized dietary regimens and life style. The proposed method can be used to monitor some parameters over a treatment period, and it can be applied for a wide range of pathologies and for studies on broader populations.

Application 2.

The exhaled breath of 14 healthy subjects (M/F 5/9, mean age 52.3, range 35-77 years) and of 12 patients (M/F 8/4, mean age 70.5, range 42-80 years) with liver cirrhosis of different class severity (The Child-Pugh class was A in 6, B in 3, and C in 3 patients) was analyzed. Real time breath analysis was performed using a buffered end-tidal (BET) on-line sampler coupled to a PTR-ToF-MS. Spectra were acquired using the data acquisition software TOF-DAQ (Tofwerk AG, Switzerland) with a mass/charge range of 10–400 Th. The data were analyzed by non-parametric ANOVA (Kruskal-Wallis test) using the Statistica 9.1 (StatSoft, USA) software. Eight compounds (2-pentanone, C8-ketone, 2 monoterpenes and 4 sulfur compounds) resulted significantly different in cirrhotic patients compared to healthy controls. Furthermore, a C8-ketone, a monoterpene and a NS-compound permitted the discrimination between Child-Pugh A and Child-Pugh B+C cirrhotic patients.

In conclusion, breath analysis allows to distinguish cirrhotic from healthy subjects and well compensated liver disease from more advanced liver stage. The proposed method can be used to identify the stage and severity of liver disease in real time with a safe and non-invasive procedure.

Final remarks and perspectives

With these two examples of applications of breath monitoring by PTR-ToF-MS we demonstrated the feasibility of an easy and fast on-line procedure for breath analysis applicable both in animals and humans. The PTR-ToF-MS allows the screening and monitoring of virtually hundreds of compounds, being capable of acquire a full spectrum in a split second, and thus not limited to few pre-selected trace ions. The analytical information entangled in the recorded spectra and extracted with *ad hoc* procedure brought to the identification of compounds related to liver disease and to the physiological state of subject as influenced by the diet. We believe that the new PTR-MS configuration will boost the research in the field of breath analysis for the identification of markers of diseases and will provide a useful tool for nutrigenomic investigations.

References

[1] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, et al., A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), International Journal of Mass Spectrometry. 286 (2009) 122–128.

[2] L. Cappellin, F. Biasioli, A. Fabris, E. Schuhfried, C. Soukoulis, T. Mark, et al., Improved mass accuracy in PTR-TOF-MS: Another step towards better compound identification in PTR-MS, International Journal of Mass Spectrometry. 290 (2010) 60–63.

[3] L. Cappellin, F. Biasioli, E. Schuhfried, C. Soukoulis, T.D. Märk, F. Gasperi, Extending the dynamic range of proton transfer reaction time-of-flight mass spectrometers by a novel dead time correction, Rapid Communications in Mass Spectrometry. 25 (2011) 179–183.

[4] L. Cappellin, F. Biasioli, P.M. Granitto, E. Schuhfried, C. Soukoulis, F. Costa, et al., On data analysis in PTR-TOF-MS: From raw spectra to data mining, Sensors and Actuators B: Chemical. 155 (2011) 183–190.

[5] E. Aprea, F. Morisco, F. Biasioli, P. Vitaglione, L. Cappellin, C. Soukoulis, et al., Analysis of breath by proton transfer reaction time of flight mass spectrometry in rats with steatohepatitis induced by high-fat diet, Journal of Mass Spectrometry. 47 (2012) 1098–1103.

[6] P. Vitaglione, F. Morisco, G. Mazzone, D.C. Amoruso, M.T. Ribecco, A. Romano, et al., Coffee reduces liver damage in a rat model of steatohepatitis: The underlying mechanisms and the role of polyphenols and melanoidins, Hepatology. 52 (2010) 1652–1661.

Physico-Chemical Advances with PTR-MS

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Abstract

We report on recent physico-chemical advances with PTR-MS, which typically involves fragmentation studies and partitioning coefficient measurements, but also desorption kinetics and and primary ion depletion phenomena.

Results and Discussion

Fragmentation Studies

First we report on fragmentation studies. This includes studies on the fragmentation behavior of mono- and di-sulfides [1], but also a specialized study on the behavior of water in the fragmentation of Allylmethylsulfide. According to quantum chemical calculations, water acts as an enhancer of the fragmentation of m/z 41 to 39 when it is present in abundance, but inhibits fragmentation when only a few water molecules are present.

Compound Identification

Moreover, we report on an alternative approach to compound identification which deploys the stickiness of compounds and takes advantage of usually disregarded measurement data [2]. To this end we investigate the desorption kinetics of sticky compounds from the inlet surface of a high-temperature-PTR-MS and find a bimodal pseudo-first order kinetics, that is concentration dependent. We develop a parameter for measuring compound specific and concentration independent the stickiness of a compound. And we show that in principle this parameter could be used to identify a compound.

Primary Ion Depletion Kinetics

Next we present an alternative method for studying fragmentation, which is complementary to E/N studies. When a lot of analyte compound is present in the drift tube, the depletion of the primary ion H_3O^+ can happen. Under these non-standard conditions, also the fragmentation pattern of the protonated analyte changes. We interpret this as a decrease in internal energies and develop this as an alternative method for fragmentation pattern analysis. By this method we are able to show the presence of adduct formation and dehydrogenation as alternative pathways of fragmentation in monosulfides. We confirm the results with traditional E/N (field strength per species) studies.

Partitioning coefficients

Last not least, we report on progress in partitioning coefficient measurements, both, on the Henry´s law constant of compounds with low solubility, and on industrially interesting partitioning coefficients.

We develop an approach to measure the Henry´s law constant (HLC) of low solubility (actually, high infinite dilution activity coefficients), such as terpenes. We account for the linear flux dependence as gas holdup, and we consider deviations there from as decreases solubility at very low fluxes, which is the result of additional partitioning of high gamma compounds. As solution for the determination of HLC we suggest an extrapolation of values from higher fluxes to zero flux. We thus determine HLC of monoterpenes and of the sesquiterpene farnesene.

Moreover, we measure the industrially interesting overall mass transfer coefficient $K_L a$. In addition we derive at the gas side and the liquid side mass transfer coefficient for monoterpenes, which demonstrates the applicability of PTR-MS to the determination of partitioning coefficients.

References

[1]   E. Schuhfried et al., Sulfides: Chemical Ionization Induced Fragmentation Studied with Proton Transfer Reaction-Mass Spectrometry Density Functional Calculations. Journal of Mass Spectrometry, in press.

[2]   E. Schuhfried et al., Desorption kinetics with PTR-MS: Isothermal differential desorption kinetics from a heterogeneous inlet surface at ambient pressure and a new concept for compound identification, International Journal of Mass Spectrometry, 314, 33-41 (2012).

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) as a rapid online tool for biogas VOCs monitoring in support of the development of Solid Oxide Fuel Cells (SOFCs)

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Abstract

We investigated biogas production with a Direct Injection Mass Spectrometry technique (PTR-MS): We produced biogas production from the Organic Fraction of Municipal Solid Waste (OFMSW), in an anaerobic dry digester. The biogas is then used to feed a Solid Oxide Fuel Cell (SOFC) generator in order to produce power and heat efficiently. The integrated biogas+SOFC solution intends to reduce pollutant gas emissions from landfilled OFMSW while fulfilling the European 20-20-20 requirements (20% energy efficiency increasing, 20% energy consumption from renewable energy, 20% greenhouse gas emissions reduction). Volatile Organic Compounds concentration, contained in the biogas fuel produced from the pilot plant, were characterized along the anaerobic digestion process and during the gas cleaning section with the Proton Transfer Reaction Time of Flight Mass Spectrometry instrument (PTR-ToF-MS). We demonstrated the monitoring capabilities of PTR-MS for biogas VOCs concentration and on the commercial filters for sulfur clean-up. Considering results from the biogas VOCs monitoring from an anaerobic digester batch, most of the tentatively identified compounds exhibited a double-peaked emission pattern, which is probably the combined result from the volatilization or oxidation of the biomass-inherited organic compounds and the microbial degradation of organic substrates. Of the sulfur compounds, hydrogen sulfide had the highest accumulative production. The results showcase the potential of the PTR-MS as fast and divers multi-channel sensor and multi-test tool in the context of online simultaneous monitoring of VOCs compounds from biogas production and from the multi-filters sample clean-up with activated carbons.

Introduction

Biogas from Anaerobic Digestion (AD) of OFMSW represents an interesting opportunity to reduce putrescible materials that otherwise would be landfilled, thus causing pollutant issues. Moreover, we set out to valorize biogas in an efficient way by producing a renewable fuel

usable for efficient power generation. Typically, the biogas produced by the anaerobic digestion batch of OFMSW consists of of 50-70% v/v methane, 30-50% v/v carbon dioxide and trace volatile compounds (Mata-Alvarez et al., 2000; Macias Corral et al., 2008). Methane, the main constituent of biogas, is formed through a complex biochemical process involving decomposition of the organic material under both anaerobic and high humidity conditions. More specifically, methane is formed via four major biochemical pathways, including: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The anaerobic digestion implemented as a post composting process is more advantageous in comparison to conventional aerobic composting for both biomass and intrinsic energy recovery. Moreover, the aerobic process of Organic Fraction of Municipal Solid Waste (OFMSW) is a highly energy-consuming process that emits large and uncontrolled amounts of volatile compounds thus raising environmental issues (Mata-Alvarez et al., 2000). A study of Desideri et al. evaluated and compared several (micro(μ)-CHP) systems to generate electrical and thermal energy; results from Cogeneration Economical Save (CES) and Primary Energy Save (PES) indexes show how SOFC systems represent the best performing solution. PES is an index introduced to compare different μ-CHP technologies with a given production of electricity and heat; whereas CES provides a figure-of-merit about the economic advantage of a system by considering both electrical and gas energy costs.

The direct use of biogas, however, may lead to cell anode damage of the SOFC after few hours of operation due to the carbon deposition and this needs to be avoided by the a proper choice of a reforming agent (Lanzini and Leone, 2010). In addition, the concentration levels of Volatile Organic Compounds (VOCs) contained in the biogas could have detrimental effects on SOFC operation (Rasmussen et al., 2011). Sulfur compounds are the most relevant trace constituents with a high impact on the cell performance as demonstrated by several studies (Rasmussen et al., 2011; Sasaki, 2008; Sasaki et al., 2011). In addition to sulfur compounds also chlorine and siloxane compounds are detrimental to the SOFC generator (Sasaki et al., 2011); chlorine and sulfur compounds affect the anode, most likely via surface adsorption blocking the Three Phase Boundary where reactive sites are placed. The presence of siloxanes can cause deposition-type degradation due to the formation of SiO_2 (s) (Sasaki et al., 2011). In general, the issues raised by waste management and fuel cleaning processing need sensitive and robust methods for the real-time analysis of the volatile compounds. More specifically an optimal filter section design is required to allow for durable SOFC power production. In this context, PTR-MS, based on an efficient implementation of chemical ionization proton transfer from hydronium ions (Biasioli et al., 2011) allows for the rapid and on-line monitoring of most volatile compounds. In this work results from Biogas VOCs characterization at the outlet of a digester pilot plant and from a gas cleaning section are presented. Sulfur compounds were used to simulate biogas pollutant compounds removal efficiency with activated carbon filters in order to better understand removal phenomena, and the gained insights are to be employed on our real pilot plant cleaning section.

Experimental Methods

Biogas characterization with PTR-ToF-MS

Dry anaerobic digestion of OFMSW was carried out in a pilot digester plant with an exploitable volume of ~16 m^3. Before loading the digester, OFMSW was mixed with chipped wood to achieve a suitable porosity aerated for four day in order to increase the temperature (up to 35 °C), allowing a rapid start-up for methane production. The biomass was thermostatically controlled by floor- and wall-fixed coils and by leachate sprinkling as well. Under these conditions the anaerobic digestion was accomplished approximately within 30

days. The biomass was subjected to a further aerobic composting treatment for 20 days before final disposal as fertilizer. Detailed monitoring of VOCs produced in the biogas were performed according to the methods described in our previous work (Papurello et al. 2012), were the biogas was sampled in (0.5 L) Nalophan bags, diluted with nitrogen gas at a ratio of 1:10 and incubated at 35 °C for 30 min using a thermostatic bath (Techne Ltd., Cambridge, UK). Methane and carbon dioxide were detected in situ by an Infrared detector (EC 322, Eco Control Milan, Italy) while oxygen was measured by an electrochemical cell (EC 322, Eco Control Milan, Italy).VOC analysis was conducted using a PTR-ToF-MS 8000 instrument in its V-mode configuration (Ionicon Analytik GmbH, Innsbruck, Austria). The sample bag content was directly injected into the drift tube of the instrument via a heated (110 °C) PEEK tube inlet. The sampling time per channel of the ToF was 0.1 ns amounting to about 350000 channels for a mass spectrum up to m/z 400 under drift tube conditions of 600 V, 2.25 mbar and 110 °C achieving an E/N ratio of about 155 Td. For every sample 30 average spectra have been acquired corresponding to a measurement time of 30 s.

VOCs cleaning section

To detect in real-time and with a high reliability VOCs that elute from the filter the same PTR-ToF-MS instrument as descirbed was employed, in order to simulate the biogas cleaning section. Experimental tests were performed with activated carbon filters, fed by a gas cylinder containing VOCs of interest through mass flow controllers. Carbon cartridges were prepared with Teflon tubes (40 mm long and 6 mm in diameter) (Swagelok Ltd, USA); 0.06 g of activated carbons were loaded in the middle of the cartridge, while a gauze sample was placed at both ends as a physical support for the carbon. In the same way, without the carbon sample, blank cartridges were prepared, which were used for reference measurements. Two commercial activated carbon catalysts: Sulfatrap R8 (TDA Research Inc., US) and Norit RGM3 (Norit, US), were used for testing VOCs removal in catalytic bed series configuration to simulate the biogas cleaning section. The catalyst have a density of 1.613 g/ml (R8) and 1.818 g/ml (RGM3), the chemical weight composition is also given for R8: Carbon <85%w, Copper oxide (I) <10%w, Copper oxide (II) <10%w, Iron oxide (III) <10%w. While for RGM3: Carbon <90 %w, Copper oxide (I) <8%w, Cr oxide <4%w. Two separated certified gas bottles (Rivoira spa, Italy), containing various concentration of VOCs (Table-1), were used to test the activated carbon cartridges.

Compound	ppmv	Molecular Weight (g/mol)
C_3H_8S	6.01	77.042
C_2H_6S	5.84	63.026
CH_4S	4.75	49.011
H_2S	5.51	34.995
C_8H_8	5.29	105.070
C_7H_8	4.83	93.070
C_4H_8O	5.10	73.065

Table 1: *VOCs contained in the cylinder gas.*

The volumetric flow was set to 120 ml/min, for sulphur compounds and 20 ml/min for aromatic and carbonyl compounds, using mass flow controllers (MKS instrument, USA). Given the mass of carbon, a gas hourly space velocity (GHSV) of 3226 h^{-1} was achieved. Tests were accomplished at ambient temperature in order to simulate the nominal conditions of the biogas production plant. To avoid a contamination of the instrument against carbon

particles, in each line where the carbon cartridges were inserted, a 50 μm polymeric membrane (PDMS) sieve was introduced.

Results and discussion

Biogas VOCs monitoring

A biogas production batch was characterized in terms of VOCs concentration, especially considering sulphur compounds that were detected and quantified, as reported in Papurello et al., 2012. In the following table a brief summary of VOCs concentration monitored along the digestion process is presented.

Test day	Sulfur ppm tot	Alcohols ppm tot	Terpenes ppm tot	Carbonyls ppm tot	Aromatics ppm tot	Chlorine compounds ppm tot	Organic nitrile ppm tot	Vocs ppm tot
1	143.66	67.23	144.28	26.96	79.56	0.11	0.44	462.25
2	1035.40	5.10	204.25	72.30	114.92	0.12	0.41	1432.50
3	974.52	1.33	195.88	90.98	97.18	0.11	0.37	1360.37
5	692.51	7.07	228.86	89.15	121.52	0.12	0.41	1139.64
15	116.23	1.42	33.10	19.07	79.90	0.11	0.21	250.04
16	59.24	0.77	20.67	14.05	49.72	0.10	0.13	144.69
19	87.47	1.39	25.35	15.69	65.63	0.11	0.17	195.80
20	92.29	0.74	17.84	18.02	73.19	0.11	0.24	202.44
21	20.74	0.77	10.18	9.37	36.78	0.08	0.09	78.02
22	2502.13	1.61	99.47	56.98	331.52	0.14	0.68	2992.51
23	2392.42	1.59	74.48	45.77	274.96	0.10	0.51	2789.85
27	2571.81	5.05	88.32	82.03	323.98	0.11	0.64	3071.94

Table 2: Biogas VOCs monitored by PTRMS.

We can identify three different time phases during biogas production:

- The first one related to the initial days of digestion in which the hydrolysis step is predominant,
- The second one in which most of the VOCs concentrations produced are stable,
- The third one where the release of terpenes, hydrogen sulphide and other sulfur compounds achieve the maximum concentration.

Qualitative and mostly quantitative analysis (Table-1) show how, in order to match biogas VOCs content with SOFC requirements, a gas cleaning section is necessary in order to remove not only sulfur compounds but also any chlorine and siloxanes. Considering sulfur compounds as the main detrimental VOCs for fuel cell generators, it can be shown from the following figure how during the first phase of digestion, mainly Methanethiol (MT) and Dimetylsulfide (DMS) have the highest concentration values, while hydrogen sulfide and propanethiol show a steep increase in concentration at the end of the digestion process thus reaching a concentration at or higher than 2000 ppmv (see Fig. 1).
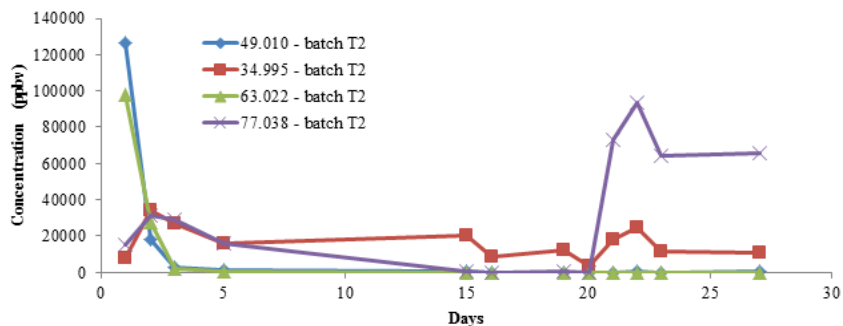
Figure. 1 - Quantitative comparison of the direct emission profiles of the predominant sulfur compounds: hydrogen sulfide (calibrated for humidity dependence), methanethiol, dimethylsulfide and propanethiol for biogas batch.

Biogas VOCs cleaning section

A gas cleaning section test was performed using the following experimental set-up:
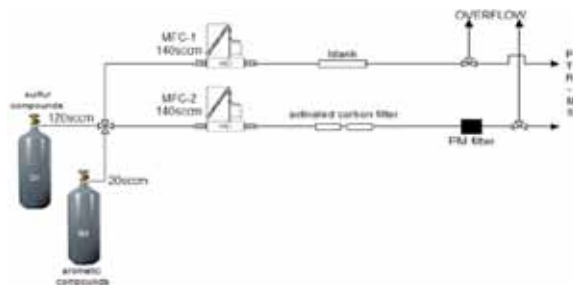
Figure 2: Experimental set-up of the gas cleaning section.

Breakthrough curves of the series bed RGM3 + R8 are shown in the following figure:
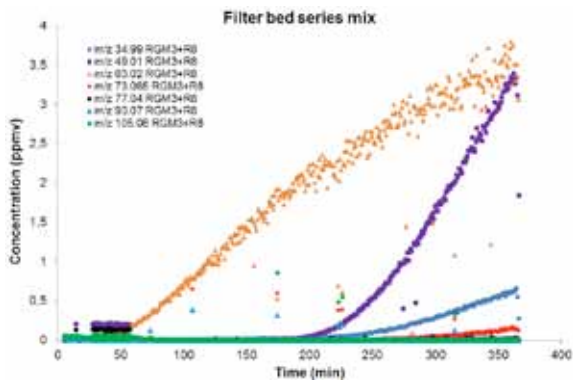
Figure 3: Breakthrough time for sulphur, aromatic and carbonyl compounds with two filters with beds in series.

Dimethylsulfide concentration is the first compound to elute from the filter bed, reaching 1 ppmv after 126 min, followed by methanethiol at 276 min. Hydrogen sulphide and the other aromatic and carbonyl compounds are well removed from the biogas with the filters. Resuming a R8 carbon sample + RGM3 carbon sample this setup was able to remove, for the 350 min of test duration, the entire concentration of xylene, propanethiol and butanethiol whereas they allow to transit of the entire concentration of DMS and MT, while only upto 10% and 9% of the initial concentration of hydrogen sulphide and butanone respectively are allowed to pass the filter.
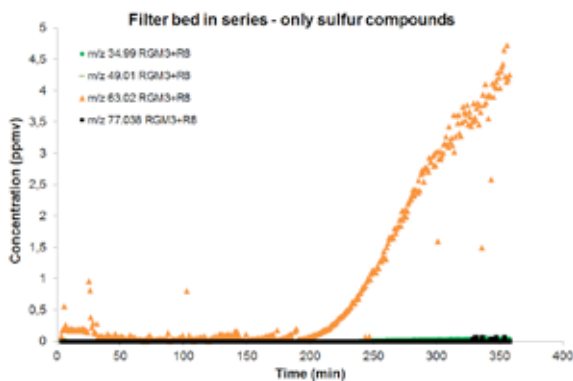
Figure 4: Breakthrough time for sulphur, compounds with two filter beds in series.

Considering only the sulphur compound contribution, assuming and simulating the absence of other VOCs in the biogas, it was observed how the breakthrough time changed. In this situation only DMS concentration achieves 1 ppmv after 226 min of test whereas none of the other compounds elute from the filter in the same time. The influence of co-pollutant compounds on breakthrough time is evident, and also the co-pollutant have to be removed efficiently from the biogas.

We demonstrated the possibility of a new method for measuring many compounds simultaneously with PTR_MS, along the anaerobic digestion process and during the gas cleaning with filters (multi-test system through the multi-port system). Moreover, this last approach allows to be run automatically with a number of filters (e.g. 20 in a single measurement). The new method adopted is rapid and very sensitive and it was experimentally demonstrated to be reliable to detect VOCs of interest to assist the energy fuel production for innovative energy production.

References

[1] Macias Corral, M., Samani, Z., Hanson, A., Smith, G., Funk, P., Yu, H., Longworth, J., 2008. Anaerobic digestion of municipal solid waste and agricultural waste and the effect of co-digestion with dairy cow manure. Bioresour. Technol. 99, 8288–8293.

[2] Mata-Alvarez, J., Mace, S., Llabres, P., 2000. Anaerobic digestion of organic solid wastes: an overview of research achievements and perspectives. Bioresour. Technol. 74, 3–16.

[3] Desideri, U., Cinti, G., Discepoli, G., Sisani, E., Penchini, D., 2012. SOFC Micro-CHP integration in residential buildings. Proceedings of ECOS 2012 - The 25th International conference on efficiency, cost, optimization, simulation and environmental impact of energy systems. June 26-29, 2012, Perugia, Italy.

[4] Lanzini, A., Leone, P., 2010. Experimental investigation of direct internal reforming of biogas in solid oxide fuel cells. Int. J. Hydrogen Energy 35, 2463–2476.

[5] Rasmussen, J.F.B., Hagen, A., Thyden, K., 2011. Durability of solid oxide fuel cells using sulfur containing fuels. J. Power Sources 196, 7271–7276.

[6] Sasaki, K., 2008. Thermochemical Stability of Sulfur Compounds in Fuel Cell Gases Related to Fuel Impurity Poisoning. J. Fuel Cell Sci. Tech., 5, 031212.

[7] Sasaki, K., Haga, K., Yoshizumi, T., Minematsu, D., Yuki, E., Liu, R., Uryu, C., Oshima, T., Ogura, T., Shiratori, Y., Ito, K.; Koyama, M., Yokomoto, K., 2011. Chemical durability of Solid Oxide Fuel Cells: Influence of impurities on long-term performance. J. Power Sources, 196, 9130–9140.

[8] Biasioli, F., Yeretzian, C., Märk, T.D., Dewulf, J., Van Langenhove, H., 2011. Direct injection mass spectrometry adds the time dimension to (B) VOC analysis. Trends Anal. Chem. 30 (7), 1003–1017.

[9] Papurello, D., Soukoulis, C., Schuhfried, E., Cappellin, L., Gasperi, F., Silvestri, S., Santarelli, M., Biasioli, F., 2012. Monitoring of volatile compound emissions during dry anaerobic digestion of the Organic Fraction of Municipal Solid Waste by Proton Transfer Reaction Time-of-Flight Mass Spectrometry. Biores. Tech., 126, 254–265.

Gap-filling of VOC flux data for deriving annual budgets: A mountain meadow case study

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Abstract

Currently the biosphere is thought to represent the main source of Volatile Organic Compound (VOC) emissions [1, 2]. Measured VOC-flux data however are mostly available for restricted time frames of several weeks during summer periods. Longer time-series of biogenic VOC measurements barely exist and if they exist they are usually fragmented. With regard to the important role of VOCs for ozone production [3] and the formation of secondary organic aerosols [4] longer time-series of VOC measurements would be extremely valuable.

As a first step towards a complete annual VOC quantification we padded times series of two nearly complete (apart from data gaps) vegetation periods of disjunct eddy covariance flux measurements of several VOCs including methanol, acetone, acetaldehyde and monoterpenes, and during the first year also isoprene and one leaf alcohol. The data set was acquired during a long-term measurement campaign above anintensively managed mountain grassland in Stubai Valley, Austria, using a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) as measurement device for the volatiles. The performance and limitations of four different gap filling approaches (linear interpolation, averaging within a moving time-window, average diurnal cycles within a moving time-window and allocation to daily classes of meteorological data) on the annual VOC balance was tested by determining errors regarding the gap filling and the variability of the resulting cumulative fluxes.

Building an average value from four approaches, the overall cumulative VOC fluxes measured above the grassland accumulated to 103 mg C m^{-2} in the year 2009 and 464 mg C m^{-2} in the year 2011, reflecting a high variability between both years. Mean errors introduced by the gap filling were calculated to be 20 mg C m^{-2} for the filling method which was performing best (average diurnal cycles with a moving time-window), while the filling method with the worst performance (linear interpolation) introduced mean errors of 34 mg C m^{-2} in 2009. The mean errors introduced by the gap filling accumulated to 13 mg C m^{-2} and 24 mg C m^{-2} in 2011 correspondingly. During both years methanol was the main compound contributing to the VOC balance. The cumulative emission fluxes for methanol (on average 375 mg C m^{-2} and 442 mg C m^{-2}), which were calculated after the application of the four different gap-filling approaches on the data, agreed within a range smaller than 7 percent in 2009 and 2 percent in 2011. In 2009 the deposition fluxes of monoterpenes turned out to have a contribution on the VOC balance which was almost as high as the contribution of methanol [5], but other compounds showed fluxes which were below 10 percent of the methanol emission flux. The cumulative flux variation for the monoterpenes was,

depending on the filling method, smaller than 10 % during the same year. The measured non-methanol VOC flux contribution was less than 5 % of the total budget in 2011.

References

[1] J. Laothawornkitkul, J. E. Taylor, N. D. Paul, and C. N. Hewitt, Biogenic volatile organic compounds in the Earth system, New Phytologist 183, 27-51, (2009).

[2] A. H. Goldstein, and I. E. Galbally, Kown and unexplored organig constituents in the earth's atmosphere, Environmental Science & Technology, 41, 1514-1521, (2007)

[3] R. Atkinson, Atmospheric chemistry of VOCs and NOx, Atmospheric Environment, 34, 2063-2101, (2011).

[4] M. Hallquist, J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J.Dommen,N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, Th. F. Mentel, A. Monod, A. S. H. Prévôt, J. H. Seinfeld, J. D. Surratt, R. Szmigielski, and J. Wildt, The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Environment, 34, 2063-2101, (2011).

[5] I. Bamberger, L. Hörtnagl, T. M.. Ruuskanen, R. Schnitzhofer, M. Müller, M. Graus, T. Karl, G. Wohlfahrt, and A. Hansel, Deposition fluxes of terpenes over grassland, Journal of Geophysical Research Atmospheres, 116(D14305), 1-13, (2011).

Proton Transfer Reaction Ion Trap Mass Spectrometry (PIT-MS) Study of a Series of Phenolic Compounds by Resonant Excitation, Collision Induced Dissociation (CID) for Applications in Flavour Science and Plant Monitoring

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Abstract

The PIT-MS built at Radboud University is a near unique instrument [1]. The ion trap mass spectrometer region of the instrument allows for many advantages over more standard quadrupole mass filter measurement techniques [2]. Namely, increased scanning speed and increased confidence in compound identification, using resonant excitation CID to perform MS/MS of selected product ions [3]. MS/MS data for Phenolic compounds, including vanillin and methyl salicylate, are presented with special reference made to the role of each compound's chemical structure in analysing their fragmentation pattern. Phenolic compounds are important compounds in flavour analysis [4, 5] and plant biology [6]. The study is of fundamental chemical interest, providing data about the structure of phenolic ions. This research will also aid in the development of a CID database for compound identification, ultimately leading to the utilization of fragmentation patterns as a method in compound identification. The study will explore the CID advantages of PIT-MS and provide information of use to researchers in flavour science and plant monitoring studies and will also be of interest to any, more general, user of PTR-MS.

Introduction

PTR-MS technology has always been mentioned as a useful tool for the monitoring of compounds where identification has been previously reported by other mass spectrometric means. The one atomic mass unit resolution of quadrupole mass filters, commonly used in PTR-MS applications, requires a lack of identification between nominally isobaric compounds i.e. compounds of the same molecular weight. The development of time of flight (TOF) mass detection systems has increased the nominal mass resolution to below a single atomic mass unit [7, 8], improving the confidence of compound identification, but not allowing a complete identification.

PIT-MS, by way of its ion trap, allows for mass and structural identification of compounds to be made. Figure 1 shows the PIT-MS set-up, where product ions formed via the reaction between H_3O^+ ions and neutral analyte are injected into the ion trap mass spectrometer from the reactor (drift tube) region. A mass scan of these ions may be performed as in a standard quadrupole mass filter, with one atomic mass unit resolution. Additionally, in ion trap mass spectrometry, a single product ion may be isolated in the trap to undergo CID.

The potential for compound identification has been explored in the PTR-MS community before [9], however standard drift tube CID of an unknown mixed gas sample will often lead to greater confusion of the spectrum, increasing the number of fragment ion from each product ion. By

individually selecting the ions for CID on a mass discrimination basis, PIT-MS can form fragment ions from a single product ion only, thus greatly simplifying identification by CID.
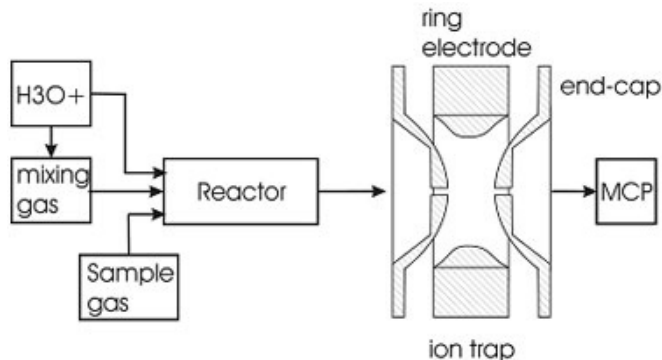
Figure 1: Block diagram of PIT-MS with additional detail showing the ion trap geometry.

References

[1] M.M.L. Steeghs, C. Sikkens, E. Crespo, S.M. Cristescu and F.J.M. Harren, Development of a proton-transfer reaction ion trap mass spectrometer: Online detection and analysis of volatile organic compounds, International Journal of Mass Spectrometry 262, 16-24, (2007).

[2] C. Warneke, J.M. Roberts, P. Veres, J. Gilman, W.C. Kuster, I. Burling, R. Yokelson and J.A. de Gouw, VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS, International Journal of Mass Spectrometry 303, 6-14, (2011).

[3] M.M.L. Steeghs, E. Crespo and F.J.M. Harren, Collision induced dissociation study of 10 monoterpenes for identification in trace gas measurements using the newly developed proton-transfer reaction ion trap mass spectrometer, International Journal of Mass Spectrometry 263, 204-212, (2007).

[4] A. Bianco, F. Buiarelli, G. Cartoni, F. Coccioli, I. Muzzalupo, A. Polidori and N. Uccella, Analysis by HPLC-MS/MS of biophenolic components in olives and oils, Analytical Letters 34, 1033-1051, (2001).

[5] B.S. Sun, M.C. Leandro, V. de Freitas and M.I. Spranger, Fractionation of red wine polyphenols by solid-phase extraction and liquid chromatography, Journal of Chromatography A 1128, 27-38, (2006).

[6] S. Gouveia, J. Goncalves and P.C. Castilho, Characterization of phenolic compounds and antioxidant activity of ethanolic extracts from flowers of Andryala glandulosa ssp varia (Lowe ex DC.) R.Fern., an endemic species of Macaronesia region, Industrial Crops and Products 42 573-582, (2013).

[7] R.S. Blake, C. Whyte, C.O. Hughes, A.M. Ellis, P.S. Monks, Demonstration of proton-transfer reaction time-of-flight mass spectrometry for real-time analysis of trace volatile organic compounds, Anaytical Chemistry 76, 3841-3845, (2004).

[8] C.J. Ennis, J.C. Reynolds, B.J. Keely and L.J. Carpenter, A hollow cathode proton transfer reaction time of flight mass spectrometer, International Journal of Mass Spectrometry 247, 72-80, (2005).

[9] W. Lindinger, A. Hansel and A. Jordan, On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research, International Journal of Mass Spectrometry and Ion Processes 173, 191-241, (1998).

Improvement in the understanding of aroma compound retention and release in naso-oro-pharyngeal cavity

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Abstract

The aim of this project was to identify the privileged sites of interactions between aromatic compounds and the lubricated mucosa of the oro-naso-pharyngeal sphere in order to better understand the phenomena of aromatic persistence. The influence of saliva and physiological parameters on aroma release was taken into account. Four experimental protocols were developed to isolate the different cavities of the oro-naso-pharyngeal sphere. For all these protocols, flavored gas enriched with various molecules with different chemical functions and physico-chemical properties was inhaled by 8 judges. The *in vivo* release of these compounds was dynamically recorded and quantified by Proton Transfer Reaction-Mass Spectrometry. Aromatic compounds seemed to interact preferentially with lubricated mouth mucosa, and very weakly with nasal mucosa. The hydrophobic ketones seemed to interact with lubricated pharyngeal mucosa. Results also showed the existence of correlations between the volumes of the oral and pharyngeal cavities and some parameters describing release kinetics. Moreover, some salivary enzymes, such as amylase, seemed to interact specifically with some aromatic molecules. These results could establish an initial advance toward the understanding of aromatic persistence phenomena.

Introduction

It is largely known that consumer choice and preferences for foods are mainly driven by their sensory properties. Among the different perceptions that occur during food consumption, aroma perception is particularly important since it starts before consuming the product (orthonasal perception), continues during the oral phase of the consumption (retronasal perception) and sometimes, can persist several minutes after the swallowing occurs. Identifying and understanding the main mechanisms explaining the release dynamics of aroma compounds responsible for sensory perceptions, considering product properties (composition, structure, etc...), individual physiology and interaction between both, constitute a real challenge for food industries [1, 2].

Aroma perception is a complex process due to the wide range of involved mechanisms (physiochemical, physiological, neurobiological, etc…), the different scales that are concerned and its dynamic dimension in relation with the consumption act. Lots of studies dealing with aroma release and perception assumed aroma compound retention by the lubricated mucosa of the oro-naso-pharyngeal cavity to explain the delayed release of some aroma compounds at the origin of persistence phenomena [1, 2]. This retention could be due to interactions of aroma compounds with the components of saliva and mucus layer (mucines, enzymes, anti-oxidant, ionic compounds, etc...) and/or with mucosa tissues themselves and seems to depend notably on aroma compound physicochemical properties. Even if the existence of these interactions is obvious,

mechanisms at the origin of these release dynamics and the role of aroma compound properties are not clearly understood. The difficulty in performing *in vivo* experiments or in developing representative *in vitro* experimental set-ups constitutes the main limits to validate or not assumptions.

The aim of the present work was to develop specific *in vivo* protocols to highlight interactions between aroma compounds and lubricated mucosa and locate them within the different compartments of the naso-oro-pharyngeal cavity.

Experimental Methods

A set of 8 molecules having different physicochemical properties and different persistence behaviours was chosen (Table 1).

Table 1: Physicochemical properties of aroma compounds used in this study (data were estimated according to US Environmental Protection Agency EPI Suite^{TM} program).

Aroma compounds	MM (g/mol)	Water solubility (25°C) (mg/L)*	Log P*	Air/water partition coefficient (25°C)*
2,5-dimethylpyrazine	108	$3.2 \ 10^4$	0.63	$1.45 \ 10^{-4}$
Diacetyl	86	10^6	-1.34	$5.45 \ 10^{-4}$
Menthol	156	435	3.40	$6.23 \ 10^{-4}$
(Z)-3-hexenol	100	$1.6 \ 10^4$	1.61	$6.35 \ 10^{-4}$
Menthone	154	181	3.05	$6.51 \ 10^{-3}$
Hexanal	100	352	1.78	$8.64 \ 10^{-3}$
2-Nonanone	142	371	3.14	$1.11 \ 10^{-2}$
Ethyl propanoate	102	$1.1 \ 10^4$	1.21	$1.26 \ 10^{-2}$

In vivo measurements were performed on 8 persons during the consumption of flavoured gaseous samples (to get rid of product effect). Concerning protocols, the locations of sample introduction (mouth or nose) and of PTR-MS measurements (mouth or nose) and swallowing or not the sample enabled to more or less expose the lubricated mucosa of different compartments (Figure 1). For protocols with swallowing (N.M.S., N.N.S. and M.M.S.), panellists were instructed to suck up gaseous samples, to keep it 5 s and then to swallow. For protocol N.N.nS., they were not allowed to swallow during 120s after sample introduction. In all cases, release data were acquired during 4 minutes. The PTR-MS instrument drift tube was thermostatically controlled (60°C) and operated at a set voltage of 600.1 ($\pm$ 0.4) V and a set pressure of 2 mbar. The 1.5 m transfer line between panellist and PTR-MS inlet was also thermostatically controlled to prevent condensation phenomena. Mass/charge ratios *m/z* 21 (signal for $H_3^{18}O^+$) and 37 (signal for water clusters H_2O-H_3O^+) were systematically monitored to check the performance of the instrument and to detect cluster ion formation. *In vivo* release kinetics curves were measured in MID mode, focusing on twelve specific masses, with a dwell time per mass of 0.1 s. Release kinetics obtained from PTR-MS measurements were characterized by the calculation of specific parameters, such as maximal intensity, time at which maximal intensity occurs, raw or standardized areas under curve or peak width. In addition to release measurements, some physiological characteristics of panelists were measured: saliva flow rate, saliva composition, mouth, nose and pharynx volumes and tidal volume. Concerning data treatment, two approaches were used to highlight protocol effect for each molecule (protocols were compared two by two) or molecule effect for a given protocol. Appropriate statistical tests (parametric and no-parametric) were used (XLStat, Addinsoft).
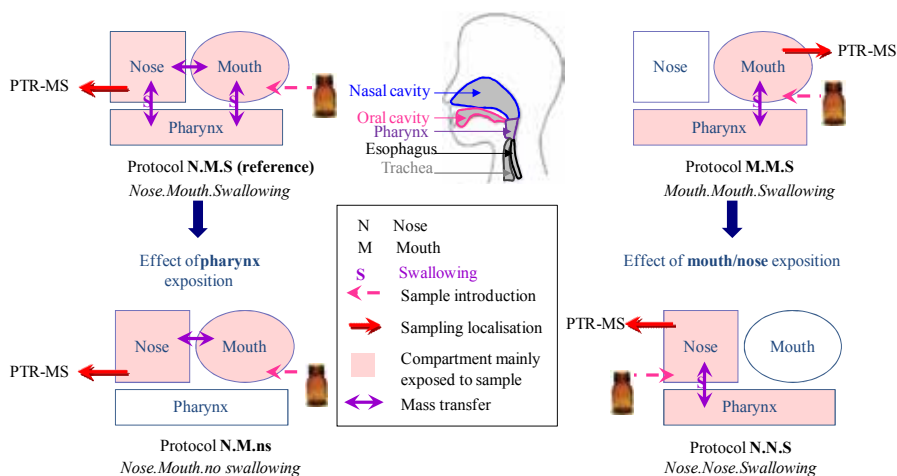
Figure 1: Schematic representation of the four protocols used in the present study.

Results

Results effectively confirmed the existence of interactions between aroma compounds and the lubricated mucosa of the naso-oro-pharyngeal cavity. These interactions appeared to depend on molecule type and properties. Persistence phenomena seemed to be mainly due to interactions with oral or pharyngeal lubricated mucosa rather than with nasal mucosa. The role of saliva, which is present in mouth and pharynx was assumed. Compounds that mainly interact with oral mucosa seemed to be 2,5-dimethylpyrazine, menthol, (Z)-3-hexenol, 2-nonanone and hexanal. Menthone and 2-nonanone, which were the two hydrophobic ketones of the set of molecules, were the only ones to present interaction with pharyngeal lubricated mucosa. Some correlations with salivary parameters such as amylase or protein concentration and with cavity volumes were observed, underlying the probable role of saliva as well as the importance of surfaces available for interaction.

In addition to molecule interaction with lubricated mucosa, others mechanisms probably influence persistence phenomena. The mechanic role of swallowing was also highlighted: it allowed mass transfer between compartments and, depending on volume cavities, can eliminate a more or less important amount of molecules from mouth.

These results constituted a first step in better understanding of phenomena at the origin of aroma release persistence and must be completed to better identify mechanisms that are involved.

References

[1] Buettner, A. and J. Beauchamp (2010). "Chemical input – Sensory output: Diverse modes of physiology–flavour interaction." Food Quality and Preference 21(8): 915-924.

[2] Doyennette, M. (2011). La bouche, un réacteur complexe à l'origine de la libération des stimuli sensoriels : modélisation des transferts de composés d'arôme lors de la déstructuration d'aliments solides. Paris, AgroParisTech: 284p.

Measuring atmospheric concentrations of formic, acetic, and butyric acids by PTR-ToFMS

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Abstract

Carboxylic acids are long-lived and persistent species in the atmosphere that have been shown to be important for the total atmospheric acidity [1]. These compounds have also been suggested as important intermediates for the formation of secondary organic aerosols [2]. Formic, acetic, and butyric acids are among the most abundant carboxylic acids in urban environments as well as in more remote areas. Observed mixing ratios range from several tens of part per billion for formic and acetic acids to a few tens of part per trillion. However, their atmospheric sources are poorly characterized due to limited measurement data. Techniques usually used to measure gas-phase concentrations of carboxylic acids suffer from low time resolution [2] and the use of fast instruments would be of prime interest to apportion the contribution of anthropogenic emissions, biogenic emissions, and photochemical processes to the carboxylic acid budget.

While PTR-MS instruments have been used to measure atmospheric concentrations of formic and acetic acids [3], only a few studies [4 and references therein] reported information about the ion chemistry driving the PTR-MS sensitivity and its dependence on operating conditions.

This study was performed to characterize a PTR-ToFMS instrument for measuring atmospheric concentrations of formic, acetic, and butyric acids. Known concentrations of carboxylic acids were generated using permeation tubes. Experiments were performed to characterize the fragmentation pattern of the parent ($RCOOHH^+$) and acylium (RCO^+) ions, sensitivities, and detection limits under various conditions of E/N. In addition, experiments were conducted at various relative humidity (RH) levels to get insights into the ion chemistry and to assess the potential impact of RH on ambient field measurements of carboxylic acids.

References

[1] A. Chebbi, and P. Carlier, Carboxylic acids in the troposphere, occurence, sources, and sinks: A review, Atmos. Env., 30, 4233-4249, (1996).

[2] R. Koppmann, Volatile Organic Compounds in the Atmosphere, Blackwell Publishing Ltd. R., (2007).

[3] J. De Gouw, and C. Warneke, Measurements of Volatile Organic Compounds in the Earth's Atmosphere Using Proton-Transfer-Reaction Mass Spectrometry, Mass Spectrometry Reviews, 26, 223-257, (2007).

[4] K. Haase, W. Keene, A. Pszenny, H. Mayne, R. Talbot, and B. Sive, Calibration and intercomparison of acetic acid measurements using proton transfer reaction mass spectrometry (PTR-MS), Atmos. Meas. Tech. Discuss., 5, 4635-4665, (2012).

Volatile organic compounds in the museum environment – a PTR-TOF pilot study on canvas samples

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Abstract

The science related to the preservation of paintings in the museum environment is in the focus of museum administrators, conservators and national authorities. A major environmental stressor to paintings is chemical exposure to organic pollutants, and in particular to organic acids. One important aspect in this context is to understand the physico-chemical interaction between organic pollutants and the painting canvas. We conducted a laboratory pilot study, in which we used a PTR-TOF 8000 instrument for real time measurements of organic trace gases in the dynamic headspace of a series of canvas samples. The experiments provided i) a characterization of the emission/desorption of volatile organic species from different canvas samples and ii) a measure of the deposition velocity of acetic acid, a common and abundant indoor pollutant, to various canvas samples. The results demonstrate the potential of the PTR-TOF technology to study organic pollutants in the museum environment.

Micro-Capillary-Column PTR-TOF

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Abstract

We demonstrate the coupling of a micro-capillary column (MCC) with a PTR-TOF MS. Like in gas chromatography a MCC provides separation of analytes, which promises discrimination between isobaric and isomeric compounds and therefore enhanced identification. Yet, the MCC setup is small enough to be installed inside the instrument and the time for a complete spectrum is only a few minutes, which allows for quasi real-time measurements in the optional MCC mode.

Introduction

Quadrupole based PTR-MS instruments have a unity mass resolution. The soft PTR ionization helps to obtain simple spectra, where a mass peak can be expected at a compound's nominal mass + 1. As a result compounds with the same nominal mass cannot be distinguished. The high mass resolving power of PTR-TOF instruments such as the Ionicon PTR-TOF 8000 is a great step towards identification of isobaric compounds, since they can be separated by their exact mass. However, the problem remains for compounds with the same molecular composition and thus same exact mass. Additional information can be gained by switching between different pre-cursor ions [1]. While this can be used to great advantage for target analysis of a certain limited number of compounds this method usually fails for complex samples, where the comparison of the spectra for different pre-cursors is too complex. Additional information on sample composition can be obtained by adding another dimension of separation to the spectrum – gas chromatography. GC separates compounds on a completely different principle [2] compared to PTR-MS. A pulse of a gaseous sample is flushed by a carrier gas stream through a GC column. The contained compounds interact with the stationary phase of the column and experience individual retention according to their physico-chemical properties. As a result the compounds exit the column separately at different retention times, which can be as long as several ten minutes. Parameters such as temperature, stationary phase material of the column, carrier gas, sample injection and gas flow, are optimized in order to best separate the compounds of interest. In standard GCs an electron impact mass spectrometer (EI-MS) or a flame ionization detector (FID) detects the peaks as they exit the column.

This idea has been implemented by several groups which have combined a gas chromatographic pre-separation with PTR-TOF-MS. For example, Lindinger et al. [3] successfully coupled the output of an external GC system with a PTR-MS. This adds more information without increasing

the complexity to the data, although online capabilities are constrained because of the long cycle period of GC measurements. Sacrificing some of the temporal resolution of a regular GC, smaller size and shorter cycle times can be gained by the use of a micro capillary column instead. These columns have already successfully been implemented with other VOC gas analyzers [4].

Here we demonstrate the first combination of a PTR-TOF-MS with an MCC. MCCs are fast enough to provide quasi real-time data and are small enough that they can be installed inside a PTR-MS instrument. Moreover, their optimal flow range is higher than for a normal single capillary column, within the range of 20-150 ml/min enabling an isothermal separation, thus simple and size-reduced construction of heating. The presented setup allows switching a PTR-MS into an MCC-mode without adaptation to the PTR-MS sampling procedure. Moreover, this setup is much cheaper and less bulky than the coupling of a commercial GC system to a PTR-TOF-MS.

Experimental Methods

In the following we will describe the parts and the setup i.e. the installation of the MCC inside a Ionicon PTR-TOF-MS 8000 (Ionicon Analytik, Innsbruck Austria) [5]. This setup can also be applied to PTR-QMS instruments, but the ability of TOF systems to measure a complete spectrum at once, is an advantage for the MCC measurement.

MCC

The multi-capillary column (S2-40/OV-1/0.2 Multichrom, Ltd) used in our setup is around 20 cm long and comprises of a bundle of 1000 parallel capillaries. The inner surface made of polydimethylsiloxane represents the stationary phase. The small length of the capillaries allows carrying out fast separations; the small inner diameters of the capillaries ensure strong interaction with the stationary phase at this short length. The large total diameter of the sum of the capillaries allows a high gas flow at low pressure. As a result, large sample volumes can be injected providing a high sensitivity mass measurement.

Sample injection

An important objective of the presented work was to implement a MCC for sample separation 1) without changing the normal operation parameters of the PTR-TOF-MS and 2) while using the normal continuous sample gas inlet.

For this purpose, we have installed a 6-port-valve which is ideally made of inert material, i.e. stainless-steel coated with Silconert2000®. The valve and the two possible positions are depicted in figure 1. A small 3-way-valve made of PEEK (Valve in fig. 1) selects the stream that is drawn towards the PTR-MS reaction chamber. In this setup the gas flow towards the reaction chamber and the pressure controller is around 50 sccm. To achieve a higher sample gas inlet flow the PTR-MS systems are equipped with an additional mass flow controller (Inlet FC). In this setup the Inlet FC can also be used for faster filling of the sample loop.

In order to control the MCC operating temperature we have installed the MCC in small aluminum housing. Peltier elements between the aluminum housing and a heat sink allow to heat AND cool the column between 40°C and 120°C. This "mini-oven" is installed directly at the outside wall of the PTR-MS climate chamber. Therefore the sample gas connections to the MCC are still cold-spot free.

Using this setup, different modes of operation can be configured:

PTR-MS mode: in the PTR-MS mode the 6-port-valve is in the position as in figure 1.a). The 3-way-valve selects the sample gas directly coming from the left side (solid line).

Sample collection mode: The sample needs to be injected into the MCC in one defined bunch. We therefore fill the so-called sample-loop by switching to the configuration in figure 1.b). The sample loop is a length of (Teflon-) tubing with a defined volume of ~ 5 ml. After a few seconds the sample loop is filled with sample gas.
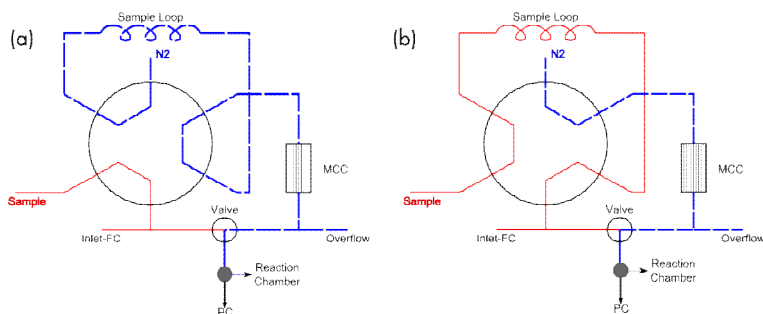

Figure 1: MCC sampling setup. The 6-port valve configuration (a) during the MCC measurement AND normal operation. (b) Configuration for filling the sample loop.

MCC mode: To measure the MCC chromatogram a short injection phase and a flushing phase is necessary. The 6-port-valve is switched back to figure 1.a). The 3-way valve selects gas from the right side (dashed line). Another mass flow controller controls (not shown in figure 1) the N_2 flow which pushes the sample through the sample loop into MCC. After a defined delay the 6-port-valve is switched back to position fig.1.b) to control the amount of sample and the initial peak width of the gas that is injected into the MCC part. The N_2 flow can be adapted to optimize the MCC measurement time and to save N_2 when it is not needed.

Results

The first data demonstrate the capabilities of the MCC-PTR-TOF. The data were collected under standard condition for the PTR-TOF and a MCC temperature of 60°C and an N_2 flow of 100 sccm.
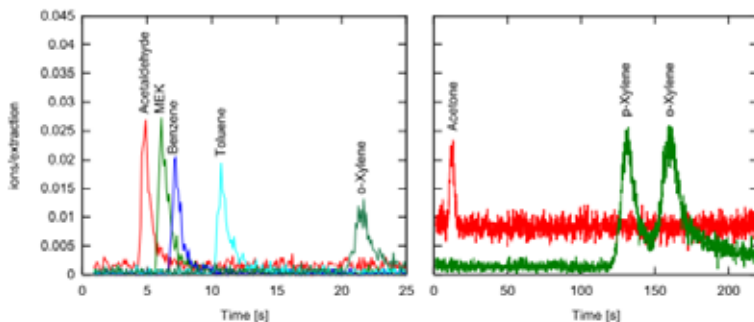

Figure 2: MCC-PTR-TOF runs. Left a mixture of compounds. Each peak appears at the compounds specific retention time, see text. (Right) the isomers p-Xylene and o-Xylene can be separated using the MCC.

The PTR-TOF is continuously measuring spectra at 10 Hz and the counts around a defined mass range are integrated to "traces", as it is common in PTR-TOF measurements. The traces of different compounds are displayed in figure 2. On this chromatogram each compound appears at its specific retention time. In a first test we measured a calibration gas mixture (VOC mix, Ionimed Analytik, Innsbruck, Austria) diluted to 200 ppbv in the MCC mode. Figure 2 shows a measurement of a standard gas mixture of Acetaldehyde, MEK, Benzene, Toluene, and o-Xylene eluted successfully within 25 seconds from the MCC. . Although, these compounds are well separated by the MCC in retention time, they are also easily separated by the high mass resolving power of the PTR-TOF alone. More interesting, however, is the separation of isobaric compounds. In figure 3 (right) we demonstrate a MCC measurement of a mixture of p- Xylene and o-Xylene. The separation of these two isomers is clearly visible.

We estimated the LOD achievable with the MCC-PTR-TOF setup so far. At a flow of 50 sccm the sample loop volume equals to an integration time of 6 seconds. The determined LOD of < 1 ppb was as expected.

Discussion

We have successfully implemented the coupling of a MCC column with a PTR-TOF system. The characteristics of the fast GC separation, i.e. fast flow, high sample volume, small dimensions, represented an ideal combination of the MCC and the PTR-TOF. We have demonstrated first of all the separation of constitutive isomers (o-Xylene and p-Xylene) in a PTR spectrum. In the presented setup, all necessary parts are installed inside the PTR-TOF-MS instrument and without alternating the normal mode of operation or the sampling procedure. It is therefore possible for the user to extract additional information by adding MCC-PTR-TOF spectra to their experiments without adapting their normal PTR-TOF sampling procedure. The MCC separation can also be used to eliminate compounds with high concentration that would hinder the measurement, e.g. ethanol in the head-space analysis of alcoholic beverages. The MCC will be offered as an add-on to Ionicon PTR-TOF systems. A tight integration of the operating modes into the PTR-TOF software, will allow the user to easily access this new feature.

References

[1] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, J.Herbig, L. Märk, R. Schottkowsky, H. Seehauser, P. Sulzer, T. D. Märk: An online ultra-high sensitivity PTR-MS combined with switchable reagent ion capability (PTR+SRI-MS), International Journal of Mass Spectrometry (2009).

[2] Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43(14), 2923–2925. doi:10.1021/jo00408a041

[3] Lindinger C., Pollien P., Ali S., Yeretzian C., Blank I., Märk T. Unambiguous identification of organic volatile compounds by PTR-MS coupled with GC/MS. Analytical Chemistry (2005), 77, 4117-4124.

[4] Ruzsanyi V. Analyse flüchtiger Metaboliten in der Ausatemluft mittels Ionenmobilitätsspektrometer. Dissertation, Universität Dortmund 2005.

[5] http://www.ionicon.com/downloads/facts_ptr-tof8000.pdf

On-line Analysis of the Coffee Roasting Process with PTR-ToF-MS: Evidence of Different Flavor Formation Dynamics for Different Coffee Varieties

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Abstract

Proton transfer reaction time of flight mass spectrometry is a powerful tool to analyse on-line processes with a high mass resolution. Here, the formation of volatile organic compounds (VOCs) during the coffee roasting process was monitored. A variation of not only the time-temperature roasting parameters (roast degree and length of roasting process) but also the variation of the coffee origin revealed changes in the coffee flavor formation: (i) different VOCs were formed differently during roasting the same type of coffee along the same time-temperature roasting profile, (ii) these formation pathways changed when changing the time-temperature roasting profile, and (iii) roasting different coffee origins led to different flavor formation pathways for the same VOCs. Roasting Colombian and Guatemalan coffee (both *coffea arabica*) led to similar formation pathways, whereas the Ethiopian coffees (Djimmah and Yirga Cheffe, both *coffea arabica*) showed different time-intensity profiles of the VOCs, as did the Indonesian *coffea canephora var. robusta* (Malangsari).

Introduction

Although coffee is known in Central Europe since the 18th century and has been studied widely, there are still several open questions regarding this famous beverage. One question is about the formation of aroma molecules during the roasting of coffee. It is well known that the way of roasting influences the flavor of a cup of coffee, either if the coffee is roasted quickly at high temperatures, or with a long time-temperature roasting profile at lower temperatures. In all cases, the green coffee beans are firstly dried during roasting, from a water content of about 10-12% to less than 5% for the roasted beans. At a certain point in the roasting process, when the temperature is high enough and the beans are dry enough, chemical reactions insight the coffee beans set in, like the Maillard reaction and the Strecker degradation, leading to the formation of the well-known aroma molecules of roasted coffee. The detailed reaction pathways, however, are not fully understood so far, as coffee beans provide a complex mixture of molecules being able to react with each other in several different ways. In addition, these reaction pathways are altering when changing the time and/or the temperature of the roasting process, making it so far impossible to predict the aroma of roasted coffee based on the green coffee and the roasting parameters. The recently developed proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS) [1], however, can at least monitor the formation pathways of the volatile organic compounds as a function of the roasting parameters, helping to understand the complex aroma formation during the coffee roasting. This has so far been done for the roasting of one type of coffee along different time-temperature roasting profiles with PTR-ToF-MS [2;3], but also with

PTR-quadrupol-MS [4;5] (although with a lower mass resolution). Additionally, studies have been performed monitoring the roasting process with laser ionization based mass spectrometry techniques [6;7]. In this study, the analysis is extended towards the roasting of coffee of different origins, namely *coffea arabica* from Colombia, Guatemala, and Ethiopia and *coffea canephora var. robusta* from Indonesia along different time-temperature roasting profiles.

Experimental Methods

PTR-ToF-MS analysis

The on-line analysis of the coffee roaster off-gas was performed with a PTR-ToF-MS 8000 (Ionicon Analytik GmbH, Austria) coupled to a drum roaster Probatino (Probat Werke, Germany, 2008, heating gas: propane, PanGAs, Winterthur) as shown in Figure 1. The coffee roasting off-gas was withdrawn with a vacuum membrane pump (Typ N86 KN.18, KNF Neuberger AG, Switzerland) through a stainless steel tube (1/4", deactivated, BGB Analytik AG, Switzerland) and diluted with activated carbon-filtered compressed air. All tubings were heated to 70°C to prevent condensation. The inlet flow of the PTR-ToF-MS was set to 100 ml/min, the drift tube temperature was 70°C. The recorded mass range was 0-310m/z.
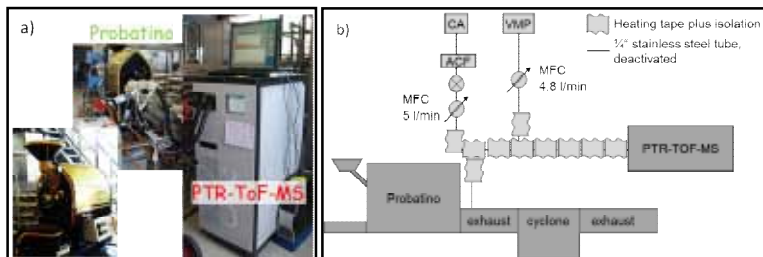

Figure 1: a) Left: Front view of the Probatino, middle: back view of the Probatino coupled to the PTR-ToF-MS (right). b) Schematics of the experimental setup. CA: compressed air; ACF: active carbon filter; VMP: vacuum membrane pump; MFC: mass flow controller.

Coffee Roasting

Green coffee beans were from Colombia (*coffea arabica*, Probat-Werke, Germany), Guatemala (Antigua La Ceiba, *coffea arabica*, Rast Kaffee AG, Switzerland), Ethiopia (Yirga Cheffe and Djimmah, *coffea arabica*, Rast Kaffee AG, Switzerland), and Indonesia (Malangsari, *coffea canephora var. robusta*, Rast Kaffee AG, Switzerland). Per roast batch 1 kg of green beans were roasted up to a defined roast degree, measured by the color of the roasted coffee beans (Colorette 3b, Probat Werke, Germany). The roasted beans were quenched with air. The time-temperature roasting profiles covered a mid-range roasting time optimal for the respective coffee (11-13 min) as well as a long term roasting (20-21 min), both to a medium roast degree of 103 Pt (filter coffee roast degree).

Results and Discussion

In Figure 2, typical mass spectra are given for the on-line analysis of the coffee roasting process. At the very beginning of the process (Figure 2a), almost no VOCs are visible (except for the intrinsic ions like $[H_3O]^+$). At the end of the roasting, shortly before the beans were removed from

the roasting drum, a huge amount of VOCs was recorded (Figure 2b), illustrating that the aroma of roasted coffee is generated during roasting. With PTR-ToF-MS, not only the mass spectra at the beginning and the end of the process can be monitored, but one is able to follow the time-intensity profile of the respective VOCs, that means the formation pathway during the roasting process. This is shown in Figure 2c for the protonated molecule $[C_5H_5O]^+$ for Colombian coffee and a 12 min time- temperature roasting profile.
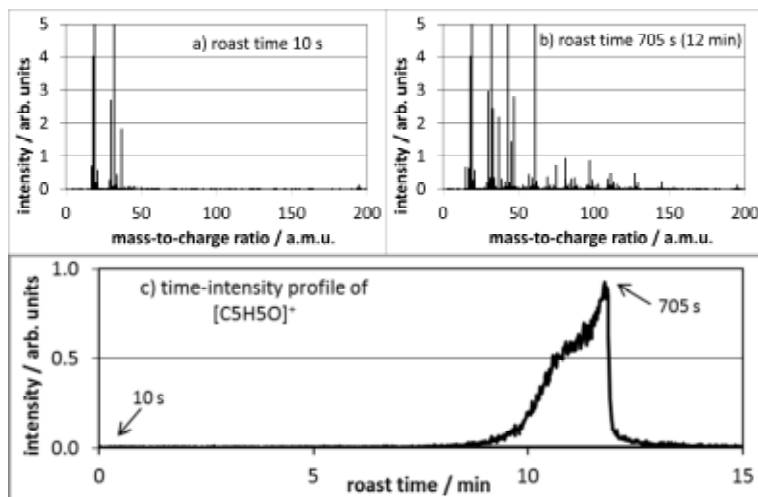

Figure 2: a) Mass spectrum at the very beginning of the roasting process at a roasting time of 10 s, b) mass spectrum at the maximum of the roasting process, after a roasting time of 705 s (12 min) and c) time-intensity profile of the VOC $[C_5H_5O]^+$.

Monitoring the same VOC, $[C_5H_5O]^+$, during the roasting of coffee from different origins, the time-intensity profiles evolved differently, as shown in Figure 3 for a 11-13 min roasting profile. Comparing, for example, the time-intensity profile of $[C_5H_5O]^+$ for Yirga Cheffe and Malangsari, this molecule is generated along completely different pathways, although both coffees were roasted along the same time-temperature profile to the same roast degree. In the case of the Ethiopian coffee, the ion was formed very intensively shortly after 10 min of roasting time, but after around 12 min, its intensity stayed more or less constant. For Malangsari, however, the intensity of $[C_5H_5O]^+$ rose very slowly but continuously up to the end of the roasting process. Comparing the Colombian coffee with the one from Guatemala, the roasting time was slightly different, but the formation pathway of the two coffees were similar. Prolonging the time-temperature roasting profile from 12 minutes to 20 minutes, a so-called long-time roasting, changed the way of aroma formation, again, as can be seen in Figure 3b for the VOC $[C_5H_5O]^+$.
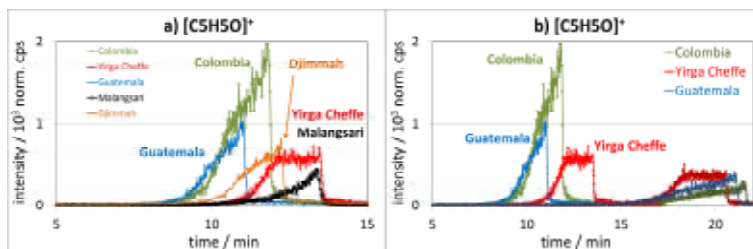
Figure 3: Time-intensity profiles of one VOC ([C_5H_5O]$^+$) during the time-temperature roasting profile of a) about 12 min and b) about 12 min and 20 min for the different coffees Colombia, Yirga Cheffe, Djimmah (only 12 min), Guatemala and Malangsari (only 13 min).

References

[1] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Maerk, H. Seehauser, R. Schottkowsky, P. Sulzer, T. D. Maerk, A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) Int.J.Mass Spec. 286, 122-128, (2009).

[2] A. N. Gloess, B. Schönbächler, A. Vietri, S. Bongers, T. Koziorowski, C. Yeretzian, Effect of roasting on the aroma of coffee. Online analysis of roasting using proton transfer reaction mass spectrometry GIT Labor-Fachzeitschrift 55, 712-715, (2011).

[3] F. Wieland, A. Gloess, M. Keller, A. Wetzel, S. Schenker, C. Yeretzian, Online monitoring of coffee roasting by proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS): towards a real-time process control for a consistent roast profile Anal.Bioanal.Chem. 402, 2531-2543, (2011).

[4] C. Yeretzian, A. Jordan, H. Brevard, W. Lindinger, On-line Monitoring of Coffee Roasting by Proton-Transfer-Reaction Mass-Spectrometry On-line Monitoring of Coffee Roasting by Proton-Transfer-Reaction Mass-Spectrometry, pp. 112-123 .

[5] C. Yeretzian, A. Jordan, R. Badoud, W. Lindinger, From the green bean to the cup of coffee: investigating coffee roasting by on-line monitoring of volatiles Eur.Food Res.Technol. 214, 92-104, (2002).

[6] R. Dorfner, T. Ferge, A. Kettrup, R. Zimmermann, C. Yeretzian, Real-time monitoring of 4-vinylguaiacol, guaiacol and phenol during coffee roasting by resonant laser ionisation time-of-flight mass-spectrometry J.Agric.Food Chem. 51 , 5768-5773, (2003).

[7] R. Dorfner, T. Ferge, C. Yeretzian, A. Kettrup, R. Zimmermann, Laser mass spectrometry as on-line sensor for industrial process analysis: Process control of coffee roasting Anal.Chem. 76, 1386-1402, (2004).

Real-time Monitoring of Trace Gas Concentrations in Syngas

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Abstract

A Proton Transfer Reaction Mass Spectrometer (PTR-MS) was used for the analysis of trace contaminations in syngas within an industrial Fischer-Tropsch process.

Introduction

In industrial gas processes the knowledge about the exact composition of the gases is important and therefore closely monitored and controlled. Trace gas impurities at much lower concentrations than the main constituents, who typically appear in percent concentrations, can play a crucial role in a Fischer Tropsch process. The poisoning effect of some impurities is a major problem in many catalytic reactions. For instance, the catalytic activity of most transition metals is drastically reduced by the presence of sulfur-containing compounds at extremely low concentration, especially for hydrogen reaction such as methanation of coal synthesis gas or reforming of naphthas [1].

Experimental Methods

A PTR-MS [2] is a gas analytical device for the sensitive detection of volatile compounds. These devices are well established in several fields of research where their capability to analyze samples in real-time yields insight into system dynamics. Examples of application of this technology are in the environmental monitoring, food and flavour science, medical and biotechnology research. Here we demonstrate the extension of the PTR-technique to the monitoring of trace compounds in syngas. In combination with a multiplexing inlet system this allows for real-time monitoring of the trace contaminations at different stages of a Fischer-Tropsch process.
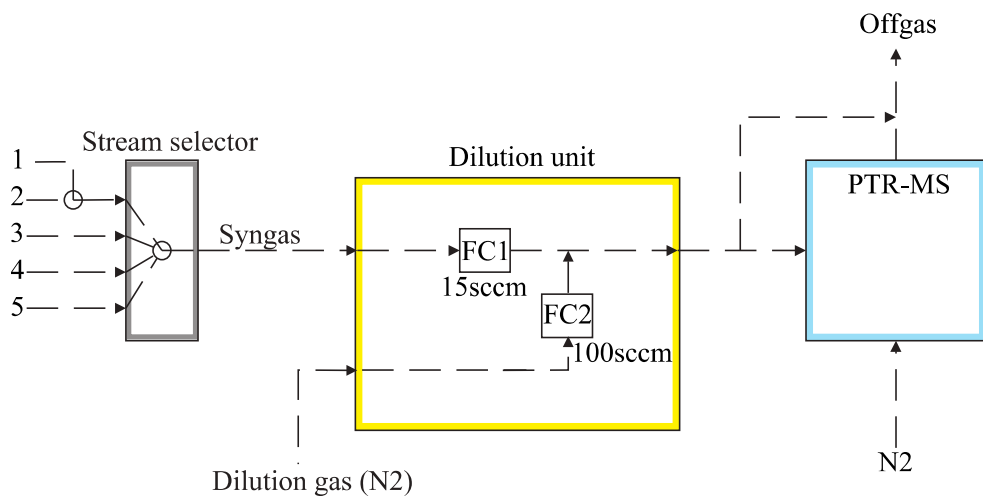
Figure 1: Schematic of the setup for the monitoring of process gas. Different streams can be selected by the stream selector. Typically, in the dilution unit 15 sccm of the process gas were diluted with 100 sccm of N_2. Approximately 80 sccm of the diluted gas were drawn into and analyzed by the PTR-MS. Figure from [3].

Results

Several volatile compounds, such as HCN, H2S, RSH, carbonyls, acids, alcohols and others) have been measured in syngas down to parts per trillion levels. The potential of this novel approach is exemplified by a filter break-through (Figure2).

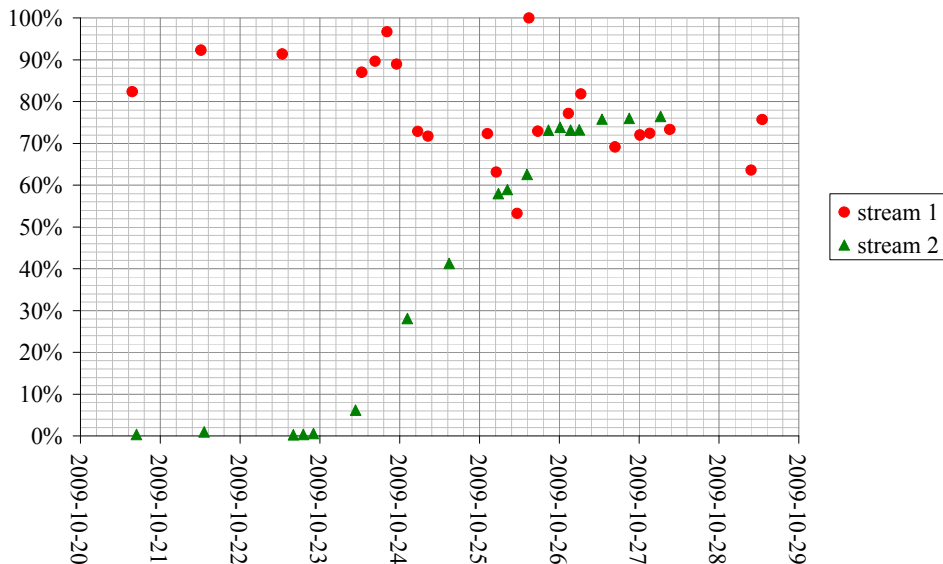*Figure3: A filter break-through can be observed after the 2009-10-22 for stream 2 while monitoring the concentration of a sulfur compound. Data is normalized to the observed maximum. Figure from [3].*

Discussion

We have employed PTR-MS for real-time monitoring of trace compounds in an industrial Fischer-Tropsch process. With minimal modifications, a PTR-MS system could be used to measure trace concentrations of several organic, inorganic and organometallic compounds in syngas. The use of a multiport valve allowed for the multiplexed measurement of trace concentrations at several different process steps.

References

[1] Oudar J. (1980) Sulfur Adsorption and Poisoning of Metallic Catalysts, *Catalysis Reviews: Science and Engineering* **22**, 2, 171-195. DOI:10.1080/03602458008066533

[2] Hansel A., Jordan A., Holzinger R., Prazeller P., Vogel W., Lindinger W. (1995) Proton transfer reaction mass spectrometry: online trace gas analysis at the ppb level, *International Journal of Mass Spectrometry and Ion Processes* **149-150**, 609-619.

[3] Herbig J.; Gutmann R.;, Winkler K.; Hansel A.; Sprachmann G., Real-time Monitoring of Trace Gas Concentrations in Syngas: Oil Gas Sci. Technol., accepted

Ambient VOC-Measurements by GC-PTR-TOF

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Abstract

Monoterpenes are important volatile organic compounds (VOC) in the atmosphere because they act as precursors of secondary organic aerosols (SOA). The SOA formation potential of monoterpenes depends on the isomere specific reactivity with OH, O_3 and NO_3. Therefore it is important to quantify the amount of monoterpene isomers separately. The recently developed PTR-TOF is able to separate isobaric compounds due to the high mass resolving power [1,2]. Isomeric VOC, however, remain undistinguishable with this technique. Therefore a Thermo-Desorption-System-Gas-Chromatograph (TDS-GC) with isomeric separation capabilities was coupled with a PTR-TOF. The performance of this new GC-PTR-TOF instrument was evaluated analyzing ambient air for several days. First results show the capability of this instrument to differentiate between monoterpene isomers at ambient levels.

Introduction

During the past 17 years PTR-MS (Proton Transfer Reaction Mass Spectrometry) became a well-established technique for real time measurements of volatile organic compounds (VOC) [1]. The recent development of PTR-TOF (Proton Transfer Reaction Time of Flight) increased the VOC separation capability due to its high mass resolution [2]. Isobaric compounds can be separated and whole mass spectra are recorded within a fraction of a second making the PTR-TOF a valuable instrument for direct eddy covariance flux measurements [3]. Isomeric VOC, however, remain undistinguishable with this technique.

Monoterpenes ($C_{10}H_{16}$) are a class of highly reactive volatile organic compounds (VOC) primarily emitted by coniferous forests, with estimated global emission rates between 32 and 127 Tg C y^{-1} [4]. Because of their role as precursors of secondary organic aerosols and their involvement in formation and growth of cloud condensation nuclei (CCN) it is important to distinguish the different monoterpene isomers. The typical OH-lifetime of α-pinene for example, is 2.6 h compared to 49 minutes for limonene under the same conditions [5].

To quantify the amount of monoterpene isomers at ambient concentrations, a Thermo-Desorption-System-Gas-Chromatograph (TDS-GC) with isomeric separation capabilities was coupled with a PTR-TOF. The performance of this new GC-PTR-TOF instrument was evaluated analyzing ambient air for several days. A comparison between the direct PTR-TOF and GC-PTR-TOF measurements showed reasonable agreement between the 2 different techniques.

Experimental Methods

Figure 1 shows the experimental setup of the GC-PTR-TOF instrument. Ambient air is pumped through an ozone-scrubber to avoid O_3-reactions on the surface of the sampling material (Tenax® TA). The ambient air is sampled by a GERSTEL "Online TDS G" consisting mainly of a "Thermo Desorption System" (TDS) and a "Cold Injection System" (CIS). The trapped VOC are then injected into the GC column ("AGILENT DB-624" 30 m, 0.32 mm, I.D. 1.8 μm), which operates with purified Nitrogen as carrier gas.

Provided that the interactions between the individual VOC and the column are different, they undergo different retardations in their transport. The detention is composed of a sequence of dynamic solution and/or adsorption equilibrium processes [6].
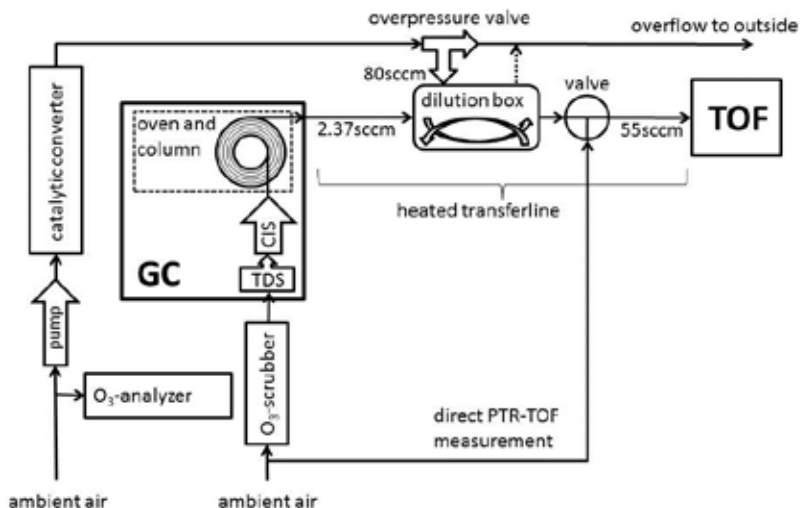

Figure 1: Experimental setup of the GC-PTR-TOF system used for continuous ambient air measurements

The measurement cycles started with simultaneous GC-sampling and direct PTR-TOF measurements of ambient air. After 15 minutes the output of the GC column was directed to the inlet of the PTR-TOF and the temporal separated VOC peaks were recorded for 45 minutes.

The calibration was conducted with the same measurement cycle using a calibration gas standard (Apel Riemer Environmental Inc., Broomfield, CO, USA) which was diluted into purified ambient air to obtain calibration gas mixtures ranging from 1 to 50 ppbv. Compound-specific sensitivities were determined from the slopes of six-point calibrations for GC-PTR-TOF as well as for direct PTR-TOF measurement.

Results

Figure 2 presents a GC-PTR-TOF chromatogram showing the signal intensity in normalized counts per second (ncps) versus retention time in seconds of the protonated exact mass 137.133 m/z (solid line) and its protonated fragment at exact mass 81.070 m/z (dashed line).

α-pinene was identified with the gas standard, the other separated monoterpenes are classified by comparison and extrapolation of retention times given in the literature [7, 8].

The GC-PTR-TOF chromatogram demonstrates the capability to separate isomeric compounds at ambient levels. We could detect 6 different monoterpene isomers in ambient air during our measurements in spring 2011.

In addition the measurements show the different break-up patterns for the different monoterpene isomers (figure 2).
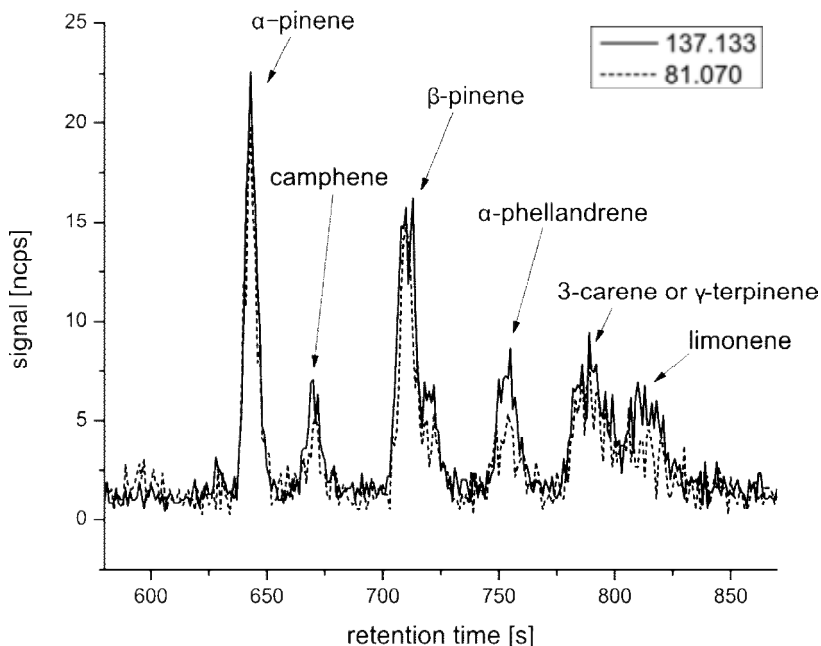

Figure 1: Separation of monoterpene isomers present in ambient air

To compare the concentrations of the direct and the GC-measurement it would be ideal to determine the individual sensitivities of the monoterpene isomers. Due to the lack of other calibration gas standards we applied the values of α-pinene for all other monoterpene isomer.

Since the direct PTR-TOF measurement does not distinguish between isomers, all different monoterpenes (α-pinene, camphene, β-pinene, α-Phellandrene, 3-carene/γ-terpinene, limonene) measured by the GC-PTR-TOF were summed to compare with the monoterpene signal measured by the PTR-TOF. During our continuous 58 h measurements mixing ratios for the sum of monoterpenes were observed as high as 0.5 to 0.8 ppbv during the night and 0.1 to 0.2 ppbv during the day. The sum of monoterpenes measured by the PTR-TOF is quantitatively in good agreement with the sum of the individual monoterpene isomers measured by the GC-PTR-TOF.

Acknowledgement

References

[1] A. Hansel, A. Jordan, R. Holzinger, P. Prazeller, W. Vogel, W. Lindinger, Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, International Journal of Mass Spectrometry 149, 609-619, (1995).

[2] M. Graus, M. Müller, A. Hansel, High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, Journal of the American Society for Mass Spectrometry 21, Issue 6, 1037-1044 , (2010).

[3] M. Mueller, M. Graus, T.M. Ruuskanen, R. Schnitzhofer, I. Bamberger, L. Kaser, T. Titzmann, L. Hoertnagl, G. Wohlfahrt, T. Karl, A. Hansel, First eddy covariance flux measurements by PTR-TOF, Atmospheric Measurement Techniques 3, Issue 2, 387-395, (2010).

[4] A. Arneth, R.K. Monson, G. Schurgers, U. Niinemets, P.I. Palmer, Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes) ? Atmospheric Chemistry and Physics, Volume 8, Issue 16, 4605-4620, (2008).

[5] R. Atkinson, J. Arey, Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmospheric Environment 37, Supplement No. 2 197–219, (2003).

[6] H. Rotzsche, Stationary Phases in Gas Chromatography, Journal of Chromatography Library, Volume 48, (1991).

[7] C. Warneke, J. de Gouw, W.C. Kuster, G.D. Goldan, R. Fall, Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method, Environmental Science and Technology, Volume 37, Issue 11, 2494-2501, (2003).

[8] D. Rood, Solvent Retention Data for DB-624 Data Sheet, Agilent Technologies, Inc., (2002), http://www.chem.agilent.com/cag/cabu/pdf/b-0292.pdf.

Interannual variability of biogenic oxygenated volatile organic compound fluxes over a managed mountain grassland

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Abstract

Volatile organic compounds (VOCs) play a complex and diverse role in atmospheric chemistry [1]. Recent technological advances gave new insights into ways how VOCs can directly or indirectly affect the chemical and physical properties of the atmosphere and into pathways and interactions that can lead to emission or deposition of specific compounds.

The development of the proton transfer reaction-mass spectrometer (PTR-MS) [2] made real-time measurements of VOC volume mixing ratios (VMRs) with concentrations as low as pptv possible. In combination with the eddy covariance method (EC) VOC fluxes can be calculated, allowing the quantification of the VOC exchange over long time periods in different ecosystems.

In the past, VOC flux research mainly focused on the highly reactive group of isoprenoids (isoprene, monoterpenes and sesquiterpenes) over forest. Especially over grassland, measurements of biogenic oxygenated volatile organic compounds (BOVOCs, e.g. methanol, acetaldehyde and acetone [3]) are still sparse and usually have been conducted over relatively short time periods of several weeks or months. Recent studies described BOVOCs to be abundant throughout the troposphere [4]. However, global estimates of their sources and sinks are still highly uncertain and little is known about the controls on BOVOC exchange and their influence on carbon budgets.

Here we present BOVOC flux measurements of methanol, acetaldehyde and acetone during the vegetation period in four years (2008-09 and 2011-12) at a managed mountain grassland near Neustift, Stubai Valley, Austria. The meadow is cut three times per year, liquid manure is brought out once, typically at the end of October. The measurement campaigns started in March of the respective year, with the exception of 2008 when measurements started two months later in May. Note that at the time of this writing the measurement campaign 2012 is still ongoing, therefore numbers given in this text are subject to change.

Methanol was the only compound to show distinct diurnal cycles throughout the four years, with maximum fluxes of up to 155.1 nmol m^{-2} s^{-1} on a half-hourly scale during the 2nd cutting of the meadow in 2012, when also the highest emission rates for acetaldehyde were recorded (16.5 nmol m^{-2} s^{-1}). The highest eflux of acetone took place during the 1st cut in 2008 (10.1 nmol m^{-2} s^{-1}).

Generally, cutting events had a dominant effect on resulting BOVOC carbon budgets due to the injured plant tissue and - as a consequence thereof - the release of compounds that were stored inside the plant.

Cumulative carbon fluxes associated with the emission of methanol were between 205.4 and 380.7 mg C m^{-2} per vegetation period, showing a net emission in all four years. The meadow also acted as a net source of acetaldehyde in each of the four vegetation periods, with emissions between 9.5 and 23.0 mg C m^{-2}. However, acetone showed a more diversified behavior. In two of the four years the meadow acted as a sink for acetone, with net uptake rates of -6.0 and -10.0 mg C m^{-2}, while the grassland was a source for acetone in 2008 with 15.5 mg C m^{-2}. The meadow was a weak sink for acetone in 2012 (-0.4 mg C m^{-2}), but as measurements are still going on at the time of this writing this could still change.

The measured total amount of carbon emitted by the meadow over the vegetation period due to BOVOC fluxes was 243.9 mg C m^{-2} in 2008 (183 days), 321.6 mg C m^{-2} in 2009 (268 days), 384.2 mg C m^{-2} in 2011 (270 days) and 324.0 mg C m^{-2} in 2012 (198 days, still ongoing). Cumulative carbon fluxes over all four years showed the meadow to be a net source of carbon associated with methanol (1217.0 mg C m^{-2}) and acetaldehyde (57.7 mg C m^{-2}), and a weak sink for acetone (-0.9 mg C m^{-2}).

References

[1] Chameides, W., R. Lindsay, J. Richardson, and C. Kiang (1988), The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, Science, 241(4872), 1473-1475, doi:10.1126/science.3420404. [online] Available from: http://www.sciencemag.org/cgi/doi/10.1126/science.3420404

[2] Lindinger, W., A. Hansel, and A. Jordan (1998), On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, International Journal of Mass Spectrometry and Ion Processes, 173(3), 191-241, doi:10.1016/S0168-1176(97)00281-4. [online] Available from: http://linkinghub.elsevier.com/retrieve/pii/S0168117697002814

[3] Seco, R., J. Peñuelas, and I. Filella (2007), Short-chain oxygenated VOCs: Emission and uptake by plants and atmospheric sources, sinks, and concentrations, Atmospheric Environment, 41(12), 2477-2499, doi:10.1016/j.atmosenv.2006.11.029. [online] Available from: http://linkinghub.elsevier.com/retrieve/pii/S135223100601168X

[4] Singh, H. B. et al. (2004), Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, Journal of Geophysical Research, 109(D15), doi:10.1029/2003JD003883. [online] Available from: http://www.agu.org/pubs/crossref/2004/2003JD003883.shtml (Accessed 24 September 2010)

A New Software Tool for the Analysis of High Resolution PTR-TOF Mass Spectra

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Abstract

The High Resolution Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (HR PTR-TOF-MS) is a powerful analytical tool used by various scientific communities for real-time measurements of volatile organic compounds (VOC). The analysis of HR PTR-TOF-MS data is, however, particularly demanding because of the large amount of complex data being generated. Based on recently developed or described mathematical methods [1-3], we have produced a new software tool, the PTR-TOF Data Analyzer, which greatly facilitates the data analysis process. Figure 1 depicts the graphical user interface of the PTR-TOF Data Analyzer in version 3.01.
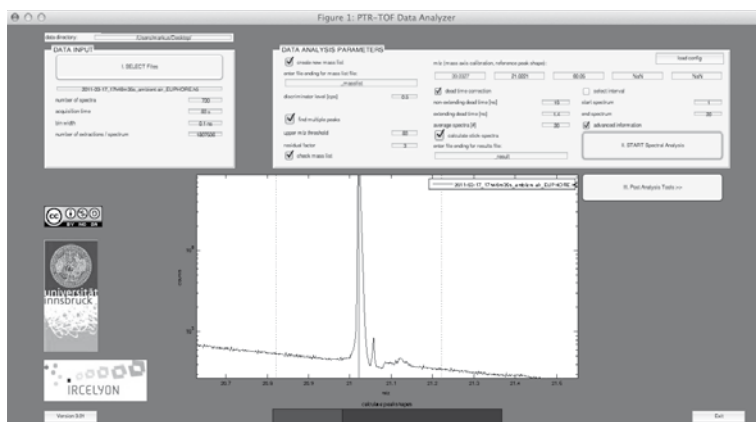
Figure 1: Graphical User Interface of the PTR-TOF Data Analyzer v3.01.

The new software solution allows for i) a combined Poisson counting statistics and dead time correction of ion count rates, ii) accurate mass axis calibration, iii) an iterative residual peak analysis that detects up to 5 isobaric peaks per unit m/z, iv) time series analysis of both low and

high mass and time resolution data, v) visualization of analysis results for fast quality assurance checks, and vi) basic post processing of result files.

Figure 2 shows exemplary data with a zoom on the mass range between m/z 57.8 to m/z 60.2. In this dataset, the PTR-TOF Data Analyzer detected two peaks at m/z 58, four peaks at m/z 59 and one peak at m/z 60. The empirical formulas were identified with a mass accuracy better than 13 ppm and were assigned as follows: m/z 58.0290 ($C_2H_4NO^+$), m/z 58.0658 ($C_3H_8N^+$), m/z 58.9826 (tentatively assigned to $CHNS^+$), m/z 59.0237 ($CH_3N_2O^+$), m/z 59.0497 ($C_3H_7O^+$), m/z 59.0693 ($C_2{}^{13}CH_8N+$), and m/z 60.0449 ($C_2H_6NO^+$).
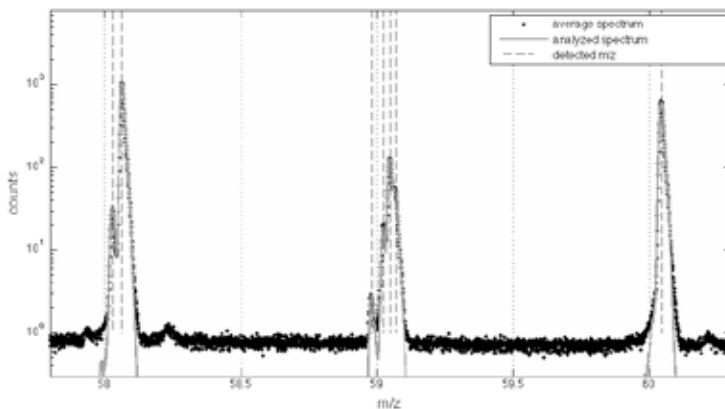

Figure 2: Visualization of all detected peaks in the mass range from m/z 57.8 to m/z 60.2. Black dots depict the average mass spectrum of all loaded spectra, dashed vertical lines the centroids of the detected peaks and the grey line the results of the iterative peak analysis.

After having been successfully tested by a group of users with different application needs, the PTR-TOF Data Analyzer is made generally available to the scientific community (https://sites.google.com/site/ptrtof/home, published under the Creative Commons license CC BY-NC-SA 3.0). This will improve the user-friendliness of the PTR-TOF-MS technique and facilitate scientific work with this new analytical mass spectrometer.

Acknowledgement

References

[1] M. Müller, M. Graus, T.M. Ruuskanen, R. Schnitzhofer, I. Bamberger, L. Kaser, T. Titzmann, L. Hörtnagl, G. Wohlfahrt, T. Karl, and A. Hansel: First eddy covariance flux measurements by PTR-TOF, Atmos. Meas. Tech., 3, 387-395, doi:10.5194/amt-3-387-2010, (2010).

[2] T. Titzmann, M. Graus, M. Müller, A. Hansel, and A. Ostermann: Improved peak analysis of signals based on counting systems: Illustrated for proton-transfer-reaction time-of-flight mass spectrometry, International Journal of Mass Spectrometry, 295, 72-77, (2010).

[3] M. Müller, C. George, and B. D'Anna: Enhanced Spectral Analysis of C-TOF Aerosol Mass Spectrometer Data: Iterative Residual Analysis and Cumulative Peak Fitting, International Journal of Mass Spectrometry, 306, 1, 1-8, doi:10.1016/j.ijms.2011.04.007, (2011).

Designer Drugs and Trace Explosives Detection with the Help of Very Recent Advancements in Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

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Abstract

At the last International PTR-MS Conference in 2011 we presented an overview of our studies on the "Detection and Identification of Illicit and Hazardous Substances with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)" including first results on explosives, chemical warfare agents and illicit and prescribed drugs detection. Since then we have considerably extended these preliminary studies to the detection of defined traces of some of the most common explosives, namely TNT, PETN, TATP, and DATP deposited into aluminum foam bodies, and to the detection of a number of novel and widely unknown designer drugs: ethylphenidate, 4-fluoroamphetamine and dimethocaine. Data from measurements of the headspace above solid standard substances are presented in order to underline these statements. The data demonstrate that PTR-MS is a versatile, sensitive and selective analytical detector for virtually all kinds of illicit and/or dangerous substances.

Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well established analytical technology in many fields of application, including environmental research [1], food and flavor science [2], and life sciences [3].

It is only recently that PTR-MS has been applied to the area of homeland security (e.g. the "Wehrwissenschaftliches Institut für Schutztechnologien" in Germany [4] and the Dstl in the UK [5]). In addition to these "end user" publications, we performed various proof-of-principle and fundamental studies on the detection capabilities of PTR-MS: explosives from small amounts of bulk samples [6], I would add the Anal. Chem. Paper here too], explosives dissolved in water [7], chemical warfare agents [8] and illicit and controlled prescription drugs [9].

Here we present data on the detection of defined trace amounts of explosives deposited into aluminum foam bodies and novel designer drugs (so called "research chemicals", which are readily available to a broad community of consumers via the internet).

Instrumental setup

For the present studies we utilized two off-the-shelf IONICON PTR-MS instruments (PTR-TOF 8000, HS PTR-QMS 500), which have been described extensively in literature. The most important operational parameter for our investigations is the reduced electric field strength E/N

(in units of Td), which is determined from the pressure, temperature, drift tube length and the voltage applied across the drift tube. By varying the E/N value (usually done by only varying the voltage) fragmentation can either be enhanced (high E/N) or suppressed (low E/N).

Results and discussion

One very recent substance in the "research chemicals scene" is ethylphenidate ($C_{15}H_{21}NO_2$), a compound very similar to methylphenidate, which is better known under the commercial name "Ritalin". Ethylphenidate is legal in most countries and produces effects such as raised alertness, mild euphoria, increased productivity, etc.

Through an internet order, we obtained a sample from a vendor in the UK and analyzed the headspace above the white crystalline powder with a PTR-TOF 8000. Surprisingly, it seems to be exceptionally pure, especially when compared to illegal drugs that are sold on the streets (purity levels of 30% or less [9]). The dominating ion is at 248.165 m/z, which is the exact mass for protonated ethylphenidate, and one "high mass" impurity (or a fragment from PTR reactions) is found at 156.081 m/z (probably $C_{11}H_{10}N^+$). In the lower mass range (i.e. 84, 75, 61, 58 m/z) we expect mainly impurities originating from solvents during the production process and preliminarily identify them via their exact mass as (protonated) $H_9C_5N^+$, $H_6C_3O_2^+$, $H_4C_2O_2^+$, $H_7C_3N^+$.

Two further designer drugs that we have studies and are reported here are dimethocaine (DC, $C_{16}H_{26}N_2O_2$) and 4-fluoroamphetamine (4-FA, $C_9H_{12}FN$). Both substances are considerably strong stimulants with DC having very similar properties to cocaine and 4-FA being more on the entactogenic side. Again, the substances were found to be surprisingly pure. In Fig. 1 we present branching ratios of DC (upper graph) and 4-FA (lower graph). DC is rather stable at all E/N values, with some fragmentation only occurring at very high E/N, while 4-FA is a nice example of a "fragile" molecule where the protonated parent ion is the most abundant ion only at very low E/N values. This information could be used to provide an unambiguous confirmation of its detection.

For our investigations of explosive traces we utilized aluminum foam bodies containing less than 1 mg of the respective explosive substances (ExploTech, Germany). The test bodies (made entirely of inorganic compounds) are mechanically impregnated with a small amount of the explosive, without using solvents, and many different types of explosives can be incorporated. The test bodies were put into glass vials and charcoal filtered air was drawn through these vials and introduced into a HS PTR-QMS 500 for analysis. From previous studies we already knew that the explosive trinitrotoluene (TNT, $C_7H_5N_3O_6$) shows a very unusual E/N behavior, i.e. the protonated parent ion shows the highest abundance at elevated E/N (reference Anal Chem paper). This behavior can be used to provide a very strong indicator that a signal at a nominal mass of 228 m/z is indeed protonated TNT and not an isobaric substance, which is not distinguishable utilizing a quadrupole based PTR-MS instrument.

As expected, the observed ion yield increases after the introduction of the test body into the vial, until equilibrium TNT concentration is reached. The signal intensity drops by nearly 50%, by reducing E/N from 150 Td to 125 Td and by nearly one order of magnitude with 100 Td. Pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$) shows a different trend. Starting with a value of 75 Td for E/N, it can be clearly seen that as soon as the E/N value is increased by 25 Td the ion yield drops significantly and disappears at 150 Td.
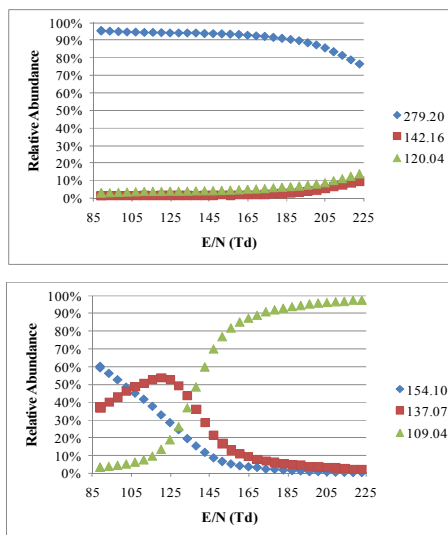
Fig. 1. Branching ratios of the "stable molecule" dimethocaine and the "fragile" molecule 4-fluoroamphetamine.

In summary, with the information about the E/N dependence of a substance we get an additional dimension for identification. With this data dimension even a low resolution quadrupole based PTR-MS instrument could be used for TNT detection with very low false positives.

Acetone peroxide (DATP, $C_6H_{12}O_4$ (dimer); TATP, $C_9H_{18}O_6$ (trimer)) is a commonly used explosive by terrorists for so-called "improvised explosive device". Fig. 2 shows that PTR-MS can easily detect TATP and DATP. At the beginning, a test body containing TATP is introduced into the vial and the substance quickly reaches equilibrium in the dynamic headspace, then the TATP test body is removed and exchanged for a DATP test body, which leads to an immediate increase in the ion yield of the protonated DATP parent.
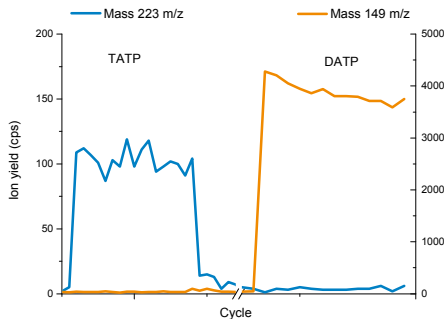

Fig. 2. Measurement of a test body containing TATP and subsequently a second test body containing DATP

In conclusion, we have demonstrated the broad applicability of PTR-MS as an analytical tool by showing its capability for detecting two completely different classes of threat agents; designer drugs and explosives. In combination with our previous publications [8, 9] this confirms our claim that PTR-MS is a versatile, sensitive and selective analytical detector for virtually all kinds of illicit and/or dangerous substances. Moreover, due to either the high mass resolution of a PTR-TOFMS or the additional information about E/N dependence, or both information combined, the risk of false positives is greatly suppressed.

Acknowledgement

References

[1] F. Biasioli, C. Yeretzian, T. D. Märk, J. Dewulf, H. Van Langenhove: Direct-injection mass spectrometry adds the time dimension to (B)VOC analysis, Trends in Analytical Chemistry 30 (7) (2011).

[2] F. Biasioli, C. Yeretzian, F. Gasperi, T. D. Märk: PTR-MS monitoring of VOCs and BVOCs in food science and technology, Trends in Analytical Chemistry 30 (7) (2011).

[3] F. Brilli, T. M. Ruuskanen, R. Schnitzhofer, M. Müller, M. Breitenlechner, V. Bittner, G. Wohlfahrt, F. Loreto, A. Hansel: Detection of Plant Volatiles after Leaf Wounding and Darkening by Proton Transfer Reaction ''Time-of-Flight'' Mass Spectrometry (PTR-TOF), PLoS ONE, 6(5) (2011), e20419.

[4] J. Ringer: Detection of Chemical Warfare Agents using Proton Transfer Reaction Mass Spectrometry. In: 5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, pp. 156-157, Innsbruck University Press, Innsbruck (2011).

[5] P. J. Hickey, S. Cairns, D. P. A. Kilgour: Towards using artificial intelligence to detect anomalies in atmospheric mass spectrometry or other spectroscopic data. In: 5th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, p. 151, Innsbruck University Press, Innsbruck (2011).

[6] C.A. Mayhew, P. Sulzer, F. Petersson, S. Haidacher, A. Jordan, L. Märk, P. Watts, T.D. Märk: Applications of proton transfer reaction time-of-flight mass spectrometry for the sensitive and rapid real-time detection of solid high explosives, International Journal of Mass Spectrometry 289 (2010), 58–63.

[7] S. Jürschik, P. Sulzer, F. Petersson, C. A. Mayhew, A. Jordan, B. Agarwal, S. Haidacher, H. Seehauser, K. Becker, T. D. Märk: Proton transfer reaction mass spectrometry for the sensitive and rapid real-time detection of solid high explosives in air and water, Anal Bioanal Chem 398 (2010), 2813–2820.

[8] F. Petersson, P. Sulzer, C.A. Mayhew, P. Watts, A. Jordan, L. Märk, T.D. Märk: Real-time trace detection and identification of chemical warfare agent simulants using recent advances in proton transfer reaction time-of-flight mass spectrometry, Rapid Commun. Mass Spectrom. 23 (2009), 3875–3880.

[9] B. Agarwal, F. Petersson, S. Jürschik, P. Sulzer, A. Jordan, T. D. Märk, P. Watts, C. A. Mayhew: Use of proton transfer reaction time-of-flight mass spectrometry for the analytical detection of illicit and controlled prescription drugs at room temperature via direct headspace sampling, Anal Bioanal Chem (2011) 400, 2631–2639.

Eddy Covariance Measurements by PTR-TOF-MS above a Ponderosa Pine Forest

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Abstract

The BEACHON (Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, 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. Here we present eddy covariance flux measurements above a ponderosa pine forest using a PTR-TOF-MS. The high time resolution of PTR-TOF-MS allowed measuring full mass spectra up to m/z 315 at 10 Hz frequency. We detected 650 different mass to charge peaks during the 30 day ambient air measurements in August 2010. Eddy covariance fluxes were calculated for all mass to charge peaks. Here we present an automated method for filtering these mass to charge peaks that show a significant flux. During the average measurement period we found 7 compounds that showed a significant flux. 2-methyl-3-butene-2-ol (MBO) dominated the emissions at this site. After a severe hailstorm we observed enhanced emissions of monoterpenes as well as for several other compounds. The emissions of the undisturbed ecosystem are compared to the emissions triggered by the physical wounding of the forest.

Introduction

Volatile Organic Compounds (VOCs) continuously emitted by anthropogenic, pyrogenic and biogenic sources can influence local and global climate due to their central role in tropospheric ozone chemistry and their ability to form aerosols [1]. Biogenic sources are considered to be ten times larger than the anthropogenic emissions [2]. PTR-MS instruments using a quadrupol mass spectrometer enabled VOC flux measurements of a selected set of compounds using disjunct eddy covariance flux measurements [3]. The recently developed PTR-TOF-MS [4,5] allows to measure the full mass spectra at 10 Hz resolution enabling direct eddy covariance measurements of the full mass range rather than just a selected set of compounds. PTR-TOF-MS flux measurements have been conducted so far above grassland [6,7,8] and above a citrus plantation [9]. Here we present the first measurements above a ponderosa pine forest.

VOC emissions by plants are mainly controlled by temperature and light. Emissions can be influenced additionally by abiotic and biotic stress factors such as drought, herbivore infestation, wounding, air pollutants and many more [10]. Most above canopy flux measurements focus on

VOC emissions of intact plants. Some studies investigated monoterpene emissions after mechanical wounding [11] others measured enhanced volume mixing ratios after storms and rain [8]. Here we also present for the first time above canopy fluxes of a forest after physical wounding due to a hailstorm.

Experimental Methods

Field Site

The BEACHON study was located at the Manitou Forest Observatory (MFO) near Woodland Park, Colorado (7500' elev., lat. 39°6'0'' N, long. 105°5'30'' W). The forest 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 soils.

Instruments

The PTR-TOF-MS sampled continuously from an about 35m long (3/8" teflon) line mounted at a tower on 25.1m close to a sonic anemometer. 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 in [4,5,6]. The data post processing was done by Matlab (Mathworks, USA) functions described by [6,7], to obtain mass spectra between m/z 17 to m/z 315. Mass scale calibration was done by adding continuously dichlorobenzene (protonated m/z 180.937) and trichlorobenzene (protonated m/z 146.976) into the PTR-TOF-MS inlet. Background measurements sampling ambient air through a catalytical converter were performed every 7 hours for 25 minutes. Instrument performance and a detailed setup during this field campaign with volume mixing ratio comparison between different instruments is given in [12].

Results and Discussion

From the 650 different mass to charge peaks 18 showed a significant flux with emissions above 0.1 mg/m^2/h. This includes protonated parent ions, fragments, isotopes and VOC-H$^+$-water clusters. These can be grouped into 7 compounds / compound classes.

The BVOC emissions from the ponderosa pine forest are dominated by 2-methyl-3-butene-2-ol (MBO). Other emission fluxes were measured for methanol, the sum of acetic acid and glycolaldehyde, the sum of acetone and propanal, monoterpenes, ethanol and acetaldehyde.

A severe hailstorm event enabled for the first time above canopy flux measurements from a disturbed ecosystem due to physical wounding. Elevated emissions of monoterpenes were measured on the days following the hailstorm. The wounding of branches and needles triggered additionally enhanced emissions of several other compounds such as sesquiterpenes, pinonaldehyde, nopinone and cymene.

Acknowledgements

References

[1] R. Koppmann, Volatile Organic Compounds in the Atmosphere, Oxford, Blackwell publishing, (2007).

[2] A. Guenther, The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, Chemosphere, 49, 837-844, (2002).

[3] T.G. Karl, C. Spirig, J. Rinne, C. Stroud, P. Prevost, J. Greenberg, R. Fall, and A. Guenther, Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 2, 279-291, (2002).

[4] M. Graus, M. Müller and A. Hansel, High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, J. Am. Soc. Mass Spectr., 21, 1037-1044, (2010).

[5] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer and T.D. Märk: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), Int. J. Mass Spectrom., 286, 122-128, (2009).

[6] M. Müller, M. Graus, T.M. Ruuskanen, R. Schnitzhofer, I. Bamberger, L. Kaser, T. Titzmann, L. Hörtnagel, G. Wohlfahrt, T. Karl, A. Hansel, First eddy covariance flux measurements by PTR-TOF, Atmos. Meas. Tech., 3, 387-398, (2010).

[7] T.M. Ruuskanen, M. Müller, R. Schnitzhofer, T. Karl, M. Graus, I. Bamberger, L. Hörtnagl, F. Brilli, G. Wohlfahrt and A. Hansel, Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, 11, 611-625, (2011).

[8] I. Bamberger, L. Hörtnagl, T.M. Tuuskanen, R. Schnitzhofer, M. Müller, M. Graus, T. Karl, G. Wohlfahrt and A. Hansel, Deposition fluxes of terpenes over grassland, J. Geophys. Res., 116, D14305, (2011).

[9] J.-H. Park, A.H. Goldstein, J. Timkovsky, S. Fares, R. Weber, J. Karlik and R. Holzinger, Eddy covariance emission and deposition flux measurements using proton-trsnafer reaction-time of flight-mass spectrometry (PTR-TOF-MS): comparison with PTR-MS measured vertical gradients and fluxes, Atmos. Chem. Phys. Discuss., 12, 20435-20482, (2012).

[10] J.K. Holopainen and J. Gershenzon, Multiple stress factors and the emission of plant VOCs, Trends Plant Sci., 15, 176-184, (2010).

[11] L. Kim, I.E. Galbally, N, Porter, I.A. Weeks and S.J. Lawson, BVOC emissions from mechanical wounding of leaves and branches of Eucalyptus sideroxylon (red ironbark), J. Atmos. Chem., 68, 265-279, (2011).

[12] L. Kaser, T. Karl, R. Schnitzhofer, M. Graus, I.S. Herdlinger-Blatt, J.P. DiGangi, B. Sive, A. Turnipseed, R.S. Hornbrook, W. Zheng, F.M. Flocke, A. Guenther, F.N. Keutsch, E. Apel and A. Hansel, Comparison of different real time VOC measurement techniques in a ponderosa pine forest, Atmos. Chem. Phys. Disc., 12, 27955-27988, (2012).

Measurement of Carbon Suboxide (C_3O_2) with PTR-TOF-MS – Atmospheric Sources and Sinks

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Abstract

There is a large volume of published studies describing the role of carbon dioxide and carbon monoxide in the atmosphere. The aim of this work was to analyze both source and sink terms of another carbon oxide, called carbon suboxide (C_3O_2), whose atmospheric relevance is yet relatively unknown. Therefore we started our studies by developing a simple method to synthesise C_3O_2 from malonic acid and phosphorous pentoxide. Afterwards a calibrated detection method was needed to identify and quantify C_3O_2 in the atmosphere. We used a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS) to monitor online in a tropical green house and ambient air in Mainz, and offline a volcanic air sample from Stromboli (Italy). Only the ambient air measurement in Mainz showed evidence of C_3O_2 in the atmosphere. First looks in biomass fire experiments show evidence of C_3O_2 and will be evaluated soon. Furthermore we studied different possibilities for C_3O_2 losses in the atmosphere. To describe the behavior of C_3O_2 on aqueous surfaces the Henry-constant ($k_H = 1.56 \pm 0.01$ M atm^{-1} at pH = 6) and hydrolysis constant ($k_{Hyd} = 0.039 \pm 0.002$ s^{-1} at pH = 6) were determined (PTR-TOF-MS). Hence, the lifetime of C_3O_2 in the presence of fog and clouds is 7 to 10 days and in the presence of aerosols is 10^4 years. In addition, the rate constants of C_3O_2 at room temperature (298±3 K) and 1000 mbar with atmospheric oxidizing agents like ozone ($k_{O3} = (1.5 \pm 0.3) \cdot 10^{-21}$ cm^3 s^{-1} molecules^{-1}) and OH radicals ($k_{OH} = (2.6 \pm 0.5) \cdot 10^{-12}$ cm^3 s^{-1} molecules^{-1}) were determined via fourier transform infrared spectrometer (FTIR) measurements. The measured UV-spectrum was used to derive the photolysis rates, in the pressure range 10 mbar to 1000 mbar and zenith angles 10° to 90°, based on model calculations.
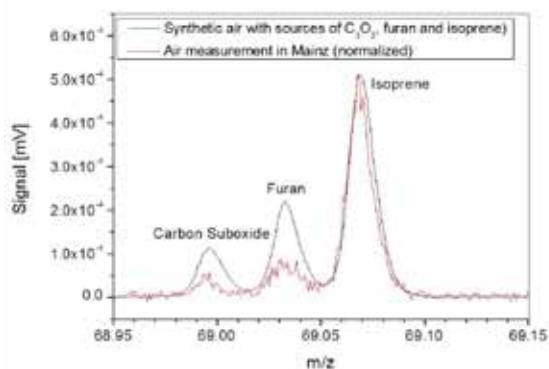
Results

Figure 1: PTR-TOF-MS measurement of synthetic air mixed with chemical sources of carbon suboxide (C_3O_2), furan (C_4H_4O) and isoprene (C_5H_8) (black line). Air measurement in Mainz (red line).
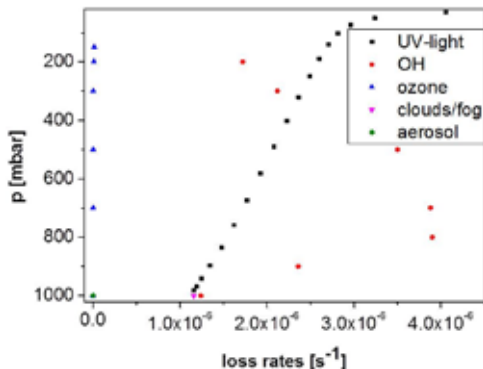

Figure 2: Atmospheric loss rates of carbon suboxide(C_3O_2)

Discussion

The atmospheric life time of carbon suboxide (C_3O_2) is of the order of approximately 10 days. It can therefore be transported hundreds of kilometers from its source which is most likely biomass burning. Upcoming results of PTR-TOF-MS measurements in biomass fire experiments will help to clarify the emission rates of C_3O_2 in the atmosphere.

The LCU: Versatile Trace Gas Calibration

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Abstract

The Ionimed Liquid Calibration Unit (LCU) evaporates aqueous standards into a gas stream, resulting in a gas flow containing compounds at defined trace concentrations. This gas can be used for calibration of trace gas analyzers over an extensive range of compounds and concentrations.

Introduction

The calibration of gas analytical devices can substantially enhance the accuracy for quantification. The classical way for trace gas calibration is to dilute a well knows gas mixture [1]. This depends on the availability of gaseous standards for the compounds of interest, which are often difficult to prepare or not commercially available.

The preparation of an aqueous standard mixture is simple, can be done immediately, and is applicable to a large variety of compounds. The LCU uses an optimized evaporation technique that can be used for volatile as well as semi-volatile compounds. The LCU is a cost efficient and highly versatile calibration device for trace gas analyzers that can be implemented in many fields of research, such as food and flavor, biotechnology, breath-gas analysis, environmental research, and petrochemical analysis. The LCU has been designed as a standalone device for the use with many different analytical trace gas analyzers; it is especially suited to calibrate Proton-Transfer-Reaction Mass-Spectrometers (PTR-MS).

Experimental Methods

Function principle

To produce trace gas concentrations of certain compounds, the Ionimed LCU evaporates a liquid standard into a gas stream at a defined rate. The liquid is nebulized to aid evaporation. The resulting micro-droplets evaporate efficiently in a heated evaporation chamber. This is depicted in figure 1, which shows the heart of the LCU, the evaporation chamber with the nebulizer.

Nebulizer

A central component of the setup is the purpose-built nebulizer (X175, Burgener Research®). The gas and liquid mix together at the tip of the nebulizer to form a fine mist. The nebulizer operates on a patented, enhanced parallel path design, which ensures less clogging, a tolerance to salts in the liquid, and smaller droplets than comparable nebulizers.
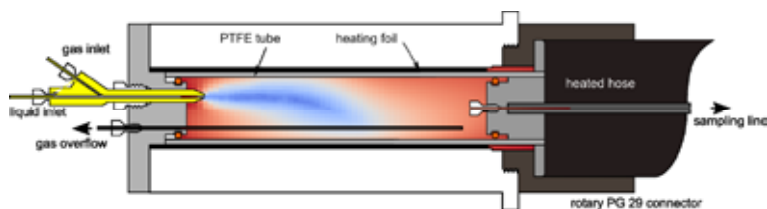
Figure 1: Schematics of the LCU. The distribution of droplets has been simulated and is visualized in the chamber.

Evaporation

The micro-droplets are ejected into a heated (> 100°C) evaporation chamber (see figure 1), which aids the evaporation process. Evaporation using micro-droplets has several advantages:

1) The evaporation of compounds with a slow rate is enhanced by the enlarged surface area of the droplets.

2) Compounds which are dissociated in water, such as acids (or bases), experience a concentration and shift in pH value when the water evaporates from a droplet. This in turn reduces the dissociation and leads to a total evaporation of the compound.

Flow Control

In a nebulizer, a gas flow (from 500 to 1000 ml/min) and liquid flow (adjustable from zero, 1.0 to 50 µl/min) are needed. For the control of the gas flow a Bronkhorst EL-Flow Digital Mass Flow Controller (MFC) is employed. The gas (clean, bottled N_2 or air) has to be connected with a pressure of > 7 barg, in order to reach the specified flow through the nebulizer's capillaries. The liquid flow mechanism has to fulfill several requirements in addition to a high stability and accuracy. The Ionimed active Liquid Flow Controller (aLFC) has been developed to meet these criteria. The aLFC has a low dead-space volume (< 100 µl), which enables rapid flushing of the flow controller. In addition, through use of a micro-pump the liquid inlet port is self-priming, i.e. the suction draws liquid samples into the LCU. All materials used are chemically inert. All flows and the chamber temperature are software controlled.

There are two versions of the LCU: a standard version (LCU-s) with 1 port for a liquid flow and 1 port for a gas flow, as described. The advanced version (LCU-a) has two liquid ports. Connecting a calibration solution on one port and clean water on the other, it is possible to run calibration steps by changing the (mixing-) ratio of the two flows while maintaining the total flow, thus keep gas humidity constant. The two flows are mixed before the nebulizer and share only a short capillary. The LCU-a has an additional gas port. The gas flow can be controlled (0, 1, … 100 ml/min) with a MFC and is directly mixed into the evaporation chamber. This allows to admix, e.g. gaseous standards (0, 1.0, … 150 ppb with 1-ppm standards) or CO_2 (0, 0.1, … 15% with pure CO_2). In order to minimize surface effects this gas port, including the MFC, is entirely coated with Silconert2000®.

Results

Example Calibrations

The key specifications and the wide-ranging applicability of the LCU have been demonstrated in trials using real-time gas analysis with PTR-MS. The LCU has been successfully used with a

growing variety of compounds, including ketones, aldehydes, alcohols, amines, terpenes, organic acids, and esters.

Figure 2 shows a calibration using an aqueous standard containing traces of acetone and acetic acid. Only the nebulization mechanism has allowed to properly evaporate acetic acid. The slower time response in the acetic acid signal is attributed to surface effects in the PTR-MS sample gas inlet line.

In figure 3 we show one calibration step with several amines and acetone. Amines are particularly prone to show surface effects, which can be seen by the slower rise in the amine signals.
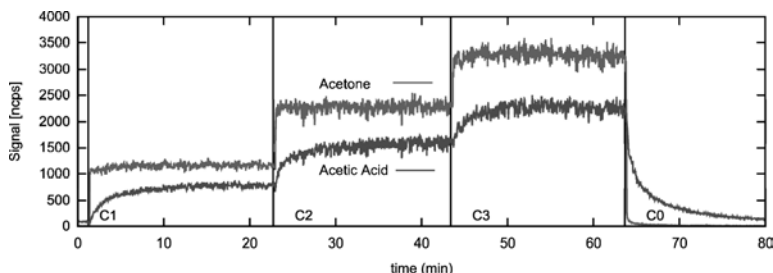

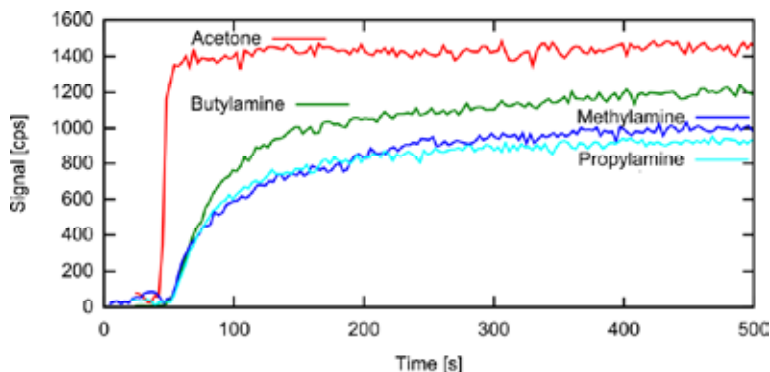Figure 2: Data of 3 calibration steps with acetone and acetic acid.

Figure 3: One calibration step with several amines and acetone as a reference.

Response Time

For the setup we determine different response times: **Calibration step:** At a gas flow of 1000 ml/min the volume in the evaporation chamber is exchanged once every 7 seconds. This dictates the lower limit for the response time and was measure to be < 20 seconds to reach stable values after the liquid flow is changed. In the GCU-a, when only the mixing ratio is changed an additional 15 seconds delay is measured, which is the time to rinse the commonly used liquid capillary. **Exchange of calibration solution:** The time needed after connecting a new standard to reach the nebulizer is around 3 minutes at a maximum flow of 50μl/min. This can be improved by using the flush mode to 1.5 min. For several compounds, semi-volatiles and those with strong surface interaction, the inlet of the analyzer was the limiting factor. More specifications can be found on [2], where we also plan to publish a list of tested compounds that will be regularly updated.

Specifications

We have determined the Precision by repeatedly performing a calibration procedure with the same and other liquid flow controllers. The precision is limited by the PTR-MS and is estimated to be < 1%. We have tested the accuracy by comparing to a gas standard using the second gas port in the LCU-a, using acetone, methanol, and acetonitrile as a reference. The determined accuracy is < 5%, and depends critically on the diligence exercised in the preparation of the liquid standard.

Aqueous Solution

A very low solubility of a compound in water is already sufficient to produce an aqueous standard. We have tested several compounds with a low solubility and also compounds with a low vapor pressure in order to test the limitations. As an example, this has been successfully achieved for propofol, which has a solubility of only 0.12 g/l (25 °C) in water. The efficient evaporation mechanism enables calibration of compounds even with very low vapor pressures (i.e. semi-volatiles). This has been successfully demonstrated for caffeine and indole, which besides its high order threshold has a low vapor pressure of only 1.6 Pa at 25 °C. These two set the current benchmark.

The upper limit for concentration ranges in the gas is the solubility and the saturation vapor pressure during evaporation and gas transport. The lower limit can be pushed towards smaller concentrations by further dilution of the standard. This will only be limited by the analyzer's LOD or the contaminations in the solvent.

Discussion

A device for the controlled evaporation of liquid samples has been demonstrated. Defined injection rates of liquid and a complete evaporation gas ensure well known VOC concentrations in the gas stream.

The LCU is ideal for compounds which have a certain minimum solubility in water. For compounds with a lower solubility, like many non-polar compounds, it is possible to use other solvents, e.g. hexane, which would require an adaptation and re-calibration of the aLFC. We will investigate different approaches, such as the use of emulsifying agents to facilitate the measurement of non-polar compounds. In additional tests, we could already show the use of a diluted Propofol emulsion, which is widely available as an aqueous emulsion.

The evaporation process is very efficient and even allows for the evaporation of semi-volatiles. This opens up the possibility to measure liquid sample with a gas analytical instrument, such as the PTR-MS. This approach is superior to head-space analysis for compounds with a low head-space concentration, like semi-volatiles or acids superior to the head-space analysis.

References

[1] Singer et al., Dynamic Gas Dilution System for Accurate Calibration of Analytical Instruments such as PTR-MS, 3rd International Conference on PTR-MS and its Applications. Eds: A. Hansel, T.D. Märk, Innsbruck University Press, pp. 232-237, (2007).

[2] www.ionimed.com/products/lcu.htm

Detection of Toxic Industrial Compounds (TIC) with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) for a real-life monitoring scenario

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Abstract

Since 2010 IONICON Analytik is a partner of the EU funded FP7-SEC project "SPIRIT"(safety and protection of built infrastructure to resist integral threats) focusing on the detection of chemical warfare agents (CWAs) and toxic industrial compounds (TICs). Most TICs are readily available, so they represent a considerable threat to security, especially when considering attacks on heating, ventilation and air conditioning (HVAC) systems in buildings. However, the existing detection technologies offer either too low sensitivity, low response time and/or insufficient selectivity to act as effective monitors.

Here we demonstrate how PTR-MS can be utilized as a selective and sensitive HVAC monitor that sets off an alarm as soon as a threat agent is present. Since quadrupole mass filter based instruments are quite cost-effective and compact, they turn out to be the instruments of choice for such applications. We present a method of how to overcome the drawbacks resulting from the limited resolution of quadrupole based instruments, in order to obtain a sufficient selectivity and thus avoiding false positive alarms.

Introduction

In the last few years we published a considerable number of studies focusing on the use of PTR-MS in detecting and analyzing different classes of threat agents and/or illicit substances. These studies range from the detection of so-called date rape drugs in different kind of beverages [1], more theoretically orientated investigations on the very unusual E/N dependence of trinitrotoluene and trinitrobenzene [2], to first results on two representative TIC compound classes, namely isocyanates and polychlorinated biphenyls [3].

IONICON's participation in the European Commission's 7th Framework Programme Collaborative Project "SPIRIT" [4] is a challenge and an opportunity to apply the whole knowledge about illicit and threat agents, which was gained in all the above-mentioned laboratory studies for the construction of a "detector and monitor for CWAs and TICs in buildings", since this is the official title of our work package and our main task within this project. One main goal was to develop a substance library for possible TICs as a function of various instrumental parameters and in particular showing the E/N dependence. In order to start such a library we performed analysis on four very toxic chemicals with high chemical priority (phosgene, diphosgene, chloroacetone, chloroacetophenone) according to the Acute Exposure Guideline

Levels (AEGL) [5]. We selected those four chemicals since all of them are readily available because of their extensive use in industry.

Here we want to present data investigating these compounds with two different kinds of PTR-MS instruments, a high resolution and high sensitivity time-of-flight based PTR-TOF 8000 and a compact quadrupole based PTR-QMS 300 instrument. We used the PTR-TOF 8000 to determine the exact masses of the ions resulting from the PTR reactions with high accuracy in order to identify their chemical compositions. In a second step we applied the findings from the PTR-TOFMS studies to a PTR-QMS instrument, since with much more compact dimensions and less instrumental weight this instrument type is more suitable for real-life monitoring [6].

Experimental Methods

A detailed description of the two utilized PTR-MS instruments can be found in in literature [e.g. 7]. The technical specifications of the PTR-TOF 8000 are a mass resolution of over 5000 m/Δm and a sensitivity of up to 250 cps/ppbv. However, these outstanding performance data come at the cost of considerable instrumental size (56x130x78 cm) and weight (about 180 kg). The PTR-QMS 300 is with 56x61x53 cm and about 80 kg much more compact and light-weight, but performs only at unit mass resolution, which makes unambiguous substance identification quite challenging.

All substances were purchased from Sigma Aldrich (Vienna, Austria): phosgene solution (20% phosgene, 80% toluene), chloroacetone (>99.8%), diphosgene (>97%), and chloroacetophenone (>98%). In order to get reasonable concentrations in the region of typical AEGLs, we sealed vials containing the individual compounds and waited for the headspace to saturate. Subsequently we drew a small amount of this saturated headspace into a gastight syringe. The content of the syringe was injected into a PTFE bag which was filled with pure nitrogen to keep the background signal low. These bags containing the trace compounds of interest were immediately connected to the PTR-MS inlet for analysis.

Results

Phosgene is presented here as one representative example of how to identify characteristic product ions (m/z ratios and corresponding intensities) with a PTR-TOF 8000

Protonated phosgene ($CCl_2O.H^+$) possesses a calculated mass of m/z 98.940 (100%) and its isotopes are visible at the masses m/z 100.937 (64%) and m/z 102.934 (10%). However, independent of the E/N value we used, this mass never was the most abundant product upon PTR ionization, as two fragments showed higher signal intensities: One fragment ion appeared at m/z 80.973 ($CClO_2H_2^+$ with the calculated mass m/z 80.974) with a ^{37}Cl isotope at m/z 82.971 (calculated m/z 82.971; 32%). The most abundant fragment ion was identified as $CClO^+$ with a calculated mass of m/z 62.963 and an isotope at m/z 64.960 (32%).

At low E/N an interesting effect can be observed: close to protonated phosgene on mass 98.940 at m/z 98.985 (Fig. 1) a second peak appears. This peak can be clearly separated from protonated phosgene and identified as $CClO_3H_4^+$ (adduction of one and two water molecules, respectively, to the most abundant fragment $CClO^+$) because of the high mass resolution and accuracy of the PTR-TOF 8000.
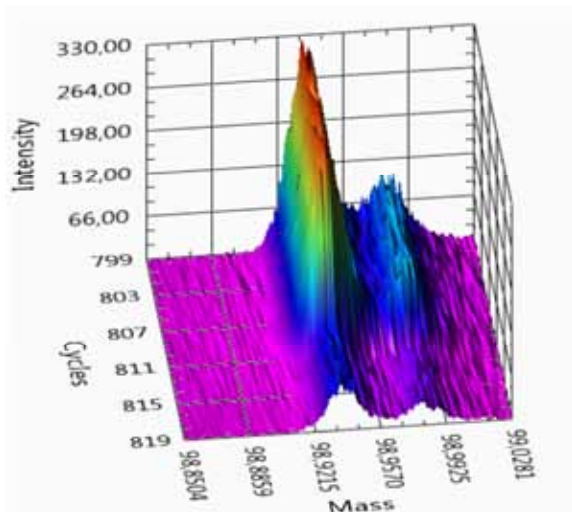
Figure 1: Protonated phosgene (m/z 98.940) which can be easily separated from the isobaric product ion $CClO_3H_4^+$ on mass m/z 98.985 with the high mass resolution of the PTR-TOF 8000.

For phosgene, the data obtained on the high resolution PTR-TOF 8000 can be used on a compact PTR-QMS in the following way: the PTR part of the (QMS) instrument is set to about 140 Td and sequentially the ion yields on nominal masses m/z 99 and 101, 81 and 83, 63 and 65 are recorded. Immediately after recoding these signals (within seconds) the detection algorithm checks if the isotopic ratios for the protonated molecule at m/z 99 compared to that at 101 (with some allowance for experimental errors and for possibilities of an interference on one of the two m/z ratios from another compound and an additional check for detector saturation). The same procedure is then repeated for the two fragment ions and the respective isotopes. If all three product ion groups match the isotopic abundance and additionally the calculated concentrations exceed a set threshold value, an alarm is triggered.

Discussion

We present data of the most characteristic product ions resulting from proton transfer reactions with important CWAs/TICs, like e.g. phosgene, chloroacetone, diphosgene, and chloroacetophenone. All measurements have been performed on a high resolution PTR-TOFMS instrument to be able to identify the exact masses of the product ions of each compound. As a next step we have implemented this "substance library" into a specialized analysis software, i.e. a computer program connected to a PTR-QMS instrument that sequentially checks for characteristic product ions at distinct E/N values (including isotopes and their ratios) and triggers an alarm as soon as the presence of one compound included in the substance library is identified and detected above a certain threshold. First successful tests utilizing such a PTR-QMS monitor were performed in summer 2012 on an HVAC test rig in the framework of the FP7-SEC project "SPIRIT". Furthermore, we hope that this real-time surveillance device will help to seriously improve safety and security in environments vulnerable to terrorist attacks with toxic chemicals.

Acknowledgement

References

[1] S. Jürschik, B. Agarwal, T. Kassebacher, P. Sulzer, C. A. Mayhew, T. D. Märk. Rapid and facile detection of four "date rape drugs" in different beverages utilizing Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). J. Mass Spectrom., 47, 1092-1097, (2012).

[2] P. Sulzer, F. Petersson, B. Agarwal, K. H. Becker, S. Jürschik, T. D. Märk, D. Perry, P. Watts, C. A. Mayhew. Proton Transfer Reaction Mass Spectrometry and the Unambiguous Real-Time Detection of 2,4,6 Trinitrotoluene. Anal. Chem.,84(9), 4161-4166, (2012).

[3] B. Agarwal, S. Jürschik, P. Sulzer, F. Petersson, S. Jaksch, A. Jordan T. D. Märk. Detection of isocyanates and polychlorinated biphenyls using proton transfer reaction mass spectrometry. Rapid Commun. Mass Spectrom., 26, 983-989, (2012).

[4] http://www.infrastructure-protection.org (7.11.2012)

[5] http://www.epa.gov/oppt/aegl/pubs/priority.htm (7.11.2012)

[6] T. Kassebacher, P. Sulzer, S. Jürschik, E. Hartungen, A. Jordan, A. Edtbauer, S. Feil, G. Hanel, S. Jaksch, L. Märk, C. A.Mayhew, T. D.Märk. Investigations of chemical warfare agents and toxic industrial compounds with proton-transfer-reaction mass spectrometry (PTR-MS) for a real-time threat monitoring scenario. Rapid Commun. Mass Spectrom., 27, 1-8, (2013).

[7] F. Biasioli, C. Yeretzian, T. D. Märk, J. Dewulf, H. Van Langenhove. Direct-injection mass spectrometry adds the time dimension to (B)VOC analysis. Trends Anal. Chem., 30(7), 1003-1017, (2011).

PTR-SRI-ToF-MS analysis of aroma compounds: influence of drift tube E/N ratio on sensitivity and fragmentation

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Abstract

The aim of this work was to compare detection and fragmentation patterns of aroma compounds obtained with three different precursor ions and several E/N source parameter values with the proton transfer reaction (PTR-MS) methodology. The reactant ions H_3O^+, NO^+ and $O_2^{+\cdot}$ were generated in a Switchable Reagent Ions (SRI) source of a PTR-ToF-MS (Ionicon 8000, Innsbruck, Austria). Precursor ions plasmas were characterized at different E/N ratio in the drift tube. For proton transfer reaction, the hydronium primary ion was the most abundant ion (> 80%) for all E/N ratios above 120 Td, but the sensitivity decreased quickly with the highest E/N values. Even though NO^+ was the most abundant primary ion in the ion plasma formed from ambient air, contaminant ions were detected with high ($O_2^{+\cdot}$ and NO_2^+) or medium (H_3O^+) intensities. For $O_2^{+\cdot}$ generated from pure oxygen, $O_2^{+\cdot}$ was the main precursor ion, the presence of contaminant ions was limited to a few percent of H_3O^+ at low E/N ratios and the reactant ion production increased significantly with increasing E/N values.

The mass spectra of 12 aroma compounds belonging to various chemical classes were recorded in the three ionization modes at different E/N values. Although H_3O^+ ionization generally displayed limited fragmentation with increasing E/N ratios (essentially with acids, esters and some alcohols), the sensitivity decreased significantly with increasing E/N values, mainly above 120 Td. For NO^+ ionization, expected charge transfer or hydride abstraction reactions were in competition with proton transfer reaction due to the presence of contaminant primary ions. $O_2^{+\cdot}$ ionization, the most energetic charge transfer reaction, displayed enhanced fragmentation, not always sensitive to increasing E/N values. For both NO^+ and $O_2^{+\cdot}$ ionizations, the global sensitivity decreased significantly with increasing E/N ratios.

Introduction

Although proton transfer reaction used in PTR-MS should be considered as a soft ionization technique, fragmentations of protonated molecular ions of volatile organic compounds (VOCs) do occur. These fragmentations are compound dependent and influenced by the drift tube parameters, particularly the ratio E/N of the electric field strength E to the buffer gas number density N in the drift tube. Otherwise, the availability of a switchable reagent ions (SRI) source with a PTR-MS instrument allows ionization of VOCs with different reactant ions, namely H_3O^+, NO^+ and $O_2^{+\cdot}$, by proton transfer, charge transfer or hydride abstraction reactions, increasing the potentialities of the method. The aim of the present work was to compare detection and fragmentation patterns of some aroma compounds ionized with the three precursor ions and to evaluate the influence of the E/N ratio on these measurements.

Experimental Methods

All the experiments were conducted with a PTR-Tof-MS instrument (PTR-ToF 8000, Ionicon Analytik, Innsbruck, Austria) equipped with a SRI source. The hydronium precursor ion was produced from distilled water vapour, NO^+ was produced from ambient air and $O_2^{+\cdot}$ from pure oxygen supply (N55 quality, Air Liquide, France). The volatiles studied (butane-2,3-dione, 3-methylbutanal, butanoic acid, 3-hydroxybutan-2-one, 3-methylbutan-1-ol, dimethyl disulfide, ethyl propanoate, oct-1-en-3-ol, 2,3,5-trimethylpyrazine, nonan-2-one, ethyl hexanoate, γ-decalactone) were from Sigma-Aldrich. The data were recorded from headspace analyses of 20 mL of aqueous solutions of each aroma compound (concentration depending on the component) in 500 mL vials hermetically sealed with three-valve caps directly connected to the PTR-MS inlet. The inlet flow rate was 70 mL/min. The inlet and drift tube temperature was set at 80°C and drift tube pressure was kept between 2.2 and 2.4 mbar. Mass spectra were recorded between *m/z* 3 and *m/z* 253 in 1.08 s. E/N ratio values were varied from 80 to 190 Td.

Results and discussion

Reactant ions plasma composition

The first determination undertaken was the comparison of the influence of the drift tube E/N ratio on the pattern of the reactant ions plasma produced from water vapour, ambient air and O_2 supply. Figure 1 presents the composition of the ions plasmas of the expected H_3O^+ and $O_2^{+\cdot}$ reactant ions. "H_3O^+" plasma was essentially characterized by H_3O^+, $H_3O^+(H_2O)$ and limited amount of $O_2^{+\cdot}$ that tended to increase with increasing E/N ratio to reach a relative proportion of 10 % of the plasma for the highest E/N. The hydronium primary ion was the most abundant ion (> 80%) for all E/N ratios above 120 Td, the cluster ion $H_3O^+(H_2O)$ abundance decreasing gradually with increasing E/N to reach a negligible relative proportion for the highest values. Reactant ions production, hence sensitivity, decreased quickly with the highest E/N values.

For $O_2^{+\cdot}$ generated from pure oxygen, $O_2^{+\cdot}$ was always the main abundant precursor ion. The presence of contaminant ions was limited to a few percent of H_3O^+ and $H_3O^+(H_2O)$ particularly at low E/N ratios, together with NO^+ and NO_2^+. Abundances of these contaminant ions decreased with increasing E/N ratio. Moreover, the production of the main reactant ion increased with increasing E/N to reach a plateau above 130 Td. Even though NO^+ was the most abundant primary ion in the ion plasma formed from ambient air, contaminant ions were detected with high ($O_2^{+\cdot}$ and NO_2^+) or medium (H_3O^+) intensities with no influence of the E/N ratio on their relative abundance (data not shown). Therefore, in these conditions side ionization reactions should be anticipated when NO^+ will be used as reagent ion.

Detection and fragmentation of aroma compounds

The detection and fragmentation pattern under the influence of increasing E/N values were evaluated for twelve volatile flavour compounds belonging to various chemical classes (see experimental part) and ionized with the three reactant ions produced with the SRI source. Fragmentation was found to be compound and reactant ion dependent. Figure 2 presents the mass fragments of ethyl propanoate obtained with the reactant ions H_3O^+, NO^+ and O_2^+ for increasing E/N values and illustrates some common features of the three ionization modes.

The sensitivity (total intensity) decreased significantly with increased E/N values in the three ionization modes. For the volatiles studied, H_3O^+ appeared to be the softest ionization agent with essentially the protonated molecule MH^+ or its main fragment ($MH^+ - H_2O$ for alcohols for instance or protonated corresponding acid for esters) present in the mass spectra. NO^+ was found

to be a soft ionization agent acting by charge transfer or hydride abstraction. $O_2^{+\cdot}$ ionization, the most energetic charge transfer reaction, displayed enhanced fragmentation, often sensitive to increasing E/N values. Generally, increasing E/N values increased the fragmentation level in the three modes.
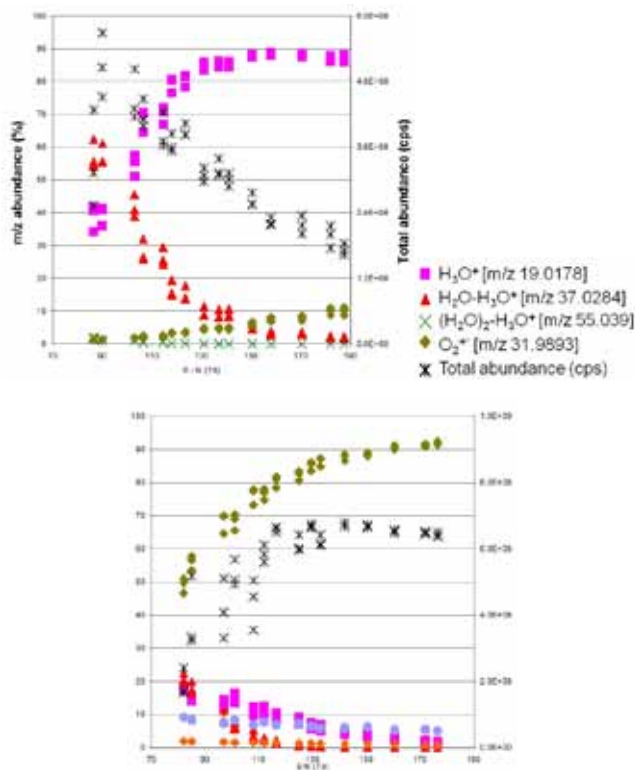

Figure 1: Reactant ions plasma composition recorded for H_3O^+ and $O_2^{+\cdot}$ ionization (n=3) with a SRI source and influence of drift tube E/N ratio. Abundances were estimated from the natural abundance of the corresponding ^{18}O isotope.

In our analyses with NO^+ and $O_2^{+\cdot}$, in addition to the expected peaks resulting essentially of charge transfers, some rather intense peaks were due to parasite proton transfer reactions because of the presence of H_3O^+ in the ion plasmas.

Prior analyses of aroma compounds appear useful to choose the optimal experimental conditions according to the type of investigations undertaken (important or negligible fragmentation needed, total intensity, resolution…). The E/N ratio applied to the drift tube can enhance or reduce the fragmentation of the analytes. Having more fragment can increase the identification chance but also the number of unidentified peaks in case of unknown mixtures. With less fragmentation the complexity of the mass spectra decreases. The SRI system allows switching between H_3O^+, NO^+ and $O_2^{+\cdot}$ reactant ions. Therefore the number of chemical compounds that can be ionized is not only limited to those with a proton affinity superior to the one of water. Analytes with an ionization potential (IP) inferior to the one of O_2 can be ionized by charge transfer from $O_2^{+\cdot}$ and

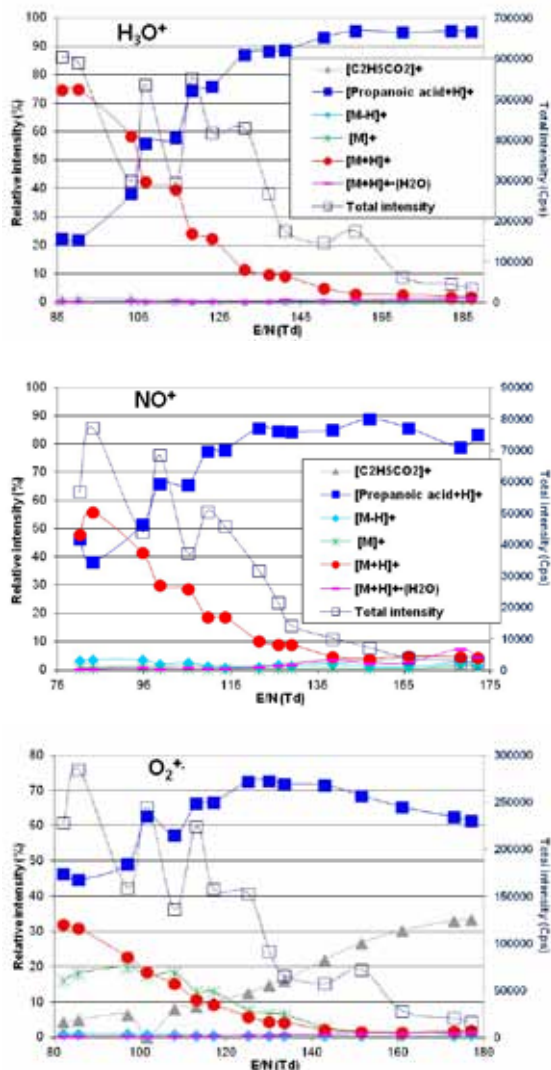those with an IP inferior to the one of NO can be ionized by charge transfer or hydride abstraction.

Figure 2: Mass fragments function of drift tube E/N ratio for ethyl propanoate ionized with the reactant ions H_3O^+, NO^+ or $O_2^{+.}$ produced in a SRI source.

Acknowledgements

Source apportionment of ambient VOCs in Belgrade semi-urban area

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Abstract

In order to assess the ambient levels, possible origin and regional transport of volatile organic compounds (VOCs), concentrations of fifteen compounds were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) together with meteorological parameters in a semi-urban site of Belgrade, Serbia during the spring of 2010. Positive Matrix Factorization (PMF) receptor model was used for VOCs sources identification and Concentration Weighted Trajectory (CWT) hybrid receptor model was applied for identification of possible source regions.

Introduction

Atmospheric residence time of volatile organic compounds (VOCs) is relatively short, from few hours to months, but the indirect impact due to their role in atmospheric chemistry is significant - the production of ozone in presence of NO_x and light, impact on OH radical concentrations and the production of photochemical oxidants as well as production of secondary aerosols. They determine global carbon cycle and global climate. It is shown that some VOCs may cause harmful health effects, from respiratory and allergic, to damage to kidney, liver and central nervous system. Because of the wide variety of impact on atmospheric processes and their adverse effects on human health, monitoring of VOCs and determination of their origin is significant.

Major anthropogenic VOCs sources in semi urban areas include fossil fuel combustion, vehicle exhaust, gasoline evaporation, industrial processes and processing of organic chemicals and organic wastes, solvent use and natural gas emissions. Benzene and toluene, associated with traffic emissions, are considered to be one of the most toxic and carcinogen VOCs. Benzene is a stable compound with lifetime of about 10 days and may be associated with both short and long range transport of traffic emission. Toluene is also present in tobacco smoke, vapors of petrol, some glue, solvents and paints, and naturally released in bush fires. Methanol, acetone and acetaldehyde may play substantial role in tropospheric chemistry as a source for OH radicals. Acetaldehyde is released into the environment during bush fires, agricultural burning, combustion of fossil fuels and produced by photochemical oxidation of other compounds in the air. Among biogenic VOCs (BVOCs), isoprene is highly reactive in lower atmosphere with atmospheric residual lifetime typically less than 1h. Beside direct emission, methyl vinyl ketone (MVK) and methacrolein (MACR) are products of isoprene photo-oxidation reaction with OH radicals.

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is a powerful tool for trace gas analysis with fast response and high detection sensitivity finding many applications in fields of atmospheric chemistry, food science, biology, medicine and process monitoring [1]. Combination of PTR-MS method with receptor models based on chemical composition makes efficient apparatus for VOC source apportionment. In this study, PMF and CWT receptor models were used for the investigation of VOCs sources and their transport processes in Belgrade.

Experimental Methods

VOCs concentrations were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) – Ionicon Analytik, Innsbruck, Austria. The measurements were performed 10 km northwest of Belgrade center (Serbia), in the semi-urban area and 100 m far from the right bank of the Danube River, 6 m above ground. 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 (E/N = 120 Td) with average H_3O^+ ion signal of $3\cdot10^6$ cps with less than 2% O_2^+. PTR-MS was programmed to monitor 15 masses at 100 ms per mass with average measurement cycle of around 4 s. These masses were selected so that the measured compounds concentrations were not dependent on humidity of the sampled air. The measured compounds either have higher proton affinity than $H^+(H_2O)_2$ clusters, so there is a direct proton transfer between cluster ion and the VOC, or they are polar and the ligand switching reactions are as efficient as the direct proton transfer. For benzene and toluene there are reports that there is very little humidity dependence of their sensitivity under given conditions in PTR-MS drift tube.

The fundamental principle of receptor modeling is that the mass conservation can be assumed and a mass balance analysis can be used for identification and apportion of VOCs sources. In order to obtain data set for modeling, individual chemical measurements can be performed at the receptor site by measuring VOCs concentrations. 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) [2] can be used to identify source tracers. For unknown emission sources, hybrid models that incorporate wind trajectories Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) can be used to resolve source locations [3]. In this study the PMF receptor model is used for source identification of VOCs and CWT for regional distribution of potential VOCs sources. Air masses back trajectories were computed by the HYSPLIT (HYbrid Single Particle Lagrangian Integrated Trajectory) model through interactive READY system. The 72-h back trajectories started from the sampling site (44.855^0 N 20.391^0 E; H_s 95 m) every hour were evaluated for three different heights above the starting point at ground level (500, 1000 and 2000) m AGL. The grid covers area of interest with cells 0.5×0.5 latitude and longitude.

Results and Discussion

VOCs concentrations measured in spring episode in 2010 are presented in Table1 (left). The most abundant were compounds with protonated masses m/z 33 (methanol) with mean concentration 10.17 ppbv, m/z 59 (acetone) 5.64 ppbv and m/z 47 (ethanol) 3.96 ppbv. Average benzene, toluene, C_8 and C_9 aromatics concentrations were not high.

In this study the PMF model has been used to analyze 1-hour averaged VOCs concentrations during measurement episode for source apportionment purpose. It generated source profiles and overall percentage source contribution estimates for source categories. Four factors were chosen as the optimum number. The profiles of the sources of VOCs are given in Table 1 (right). The first profile extracted by PMF is vehicular exhaust having high loadings of compounds with protonated masses m/z 79 (benzene), m/z 93 (toluene), m/z 107 (xylenes, C_8 aromatics) and m/z 121 (C_9 aromatics) with average contribution of 25%. The second profile has high loadings of m/z 33 (methanol), m/z 45 (acetaldehyde), m/z 59 (acetone, C3 aromatics), m/z 71 (methyl vinyl ketone, methacrolein) and m/z 73 (methyl ethyl ketone) and can be related to solvent use and painting with average contribution of 24%. The third profile related to smaller productions around the sampling site have high loadings of m/z 47 (ethanol) and m/z 59 (acetone, C_3 aromatics) with average contribution 18%.

Table 1: Statistical parameters of 1-hour mean VOCs concentrations [ppbv] measured in Belgrade semi-urban area, in the spring 2010 (left) and source profiles derived by PMF (right)

Species	Mean	Min	Max	10th Perc.	95th Perc.	Range	Std. Dev.	P1	P2	P3	P4
m/z 33 (methanol)	10.17	3.07	47.44	4.21	19.94	44.37	5.57	0	64	27	9
m/z 42 (acetonitrile)	0.33	0.13	2.16	0.18	0.60	2.03	0.19	1	18	32	50
m/z 45 (acetaldehyde)	3.71	0.92	16.93	1.68	7.38	16.00	2.07	18	36	21	25
m/z 47 (ethanol)	3.96	2.73	15.99	3.03	5.36	13.27	1.28	9	13	72	5
m/z 59 (acetone)	5.64	2.23	24.28	2.86	10.58	22.06	2.90	8	43	38	11
m/z 69 (isoprene, furan)	0.62	0.10	6.75	0.25	1.34	6.65	0.47	18	17	8	57
m/z 71(MVK, MACR)	0.65	0.10	3.34	0.24	1.38	3.23	0.40	11	40	0	49
m/z 73 (MEK)	1.45	0.33	13.22	0.56	3.48	12.90	1.18	18	59	24	0
m/z 79 (benzene)	0.97	0.17	5.55	0.35	2.44	5.38	0.74	47	0	10	43
m/z 83 (2-methylfuran)	0.48	0.08	3.56	0.21	1.06	3.48	0.31	10	21	3	67
m/z 93 (toluene)	2.17	0.23	14.70	0.55	5.76	14.47	1.96	77	11	5	6
m/z 95 (phenol)	0.31	0.06	2.94	0.13	0.65	2.88	0.24	4	2	10	84
m/z 105 (styrene)	0.18	0.03	3.24	0.08	0.41	3.21	0.19	14	17	1	68
m/z 107 (C$_8$ aromatics)	1.73	0.25	11.03	0.56	4.32	10.78	1.42	71	6	12	12
m/z 121 (C$_9$ aromatics)	0.82	0.09	5.00	0.22	2.07	4.91	0.74	69	6	2	24

The fourth profile has high loadings of m/z 83 (2-methylfuran), m/z 95 (monoterpene fragment, phenol, 2-vinilefuran) and m/z 105 (styrene), and medium loadings of m/z 42 (acetonitrile), m/z 69 (isoprene, furan), m/z 71 (MVK, methyl vinyl ketone, methacrolein) and m/z 79 (benzene), which can be related to biomass/biofuels burning, with average contribution of 36%. The identified source contribution time series plots are presented on Figure 1 (left).
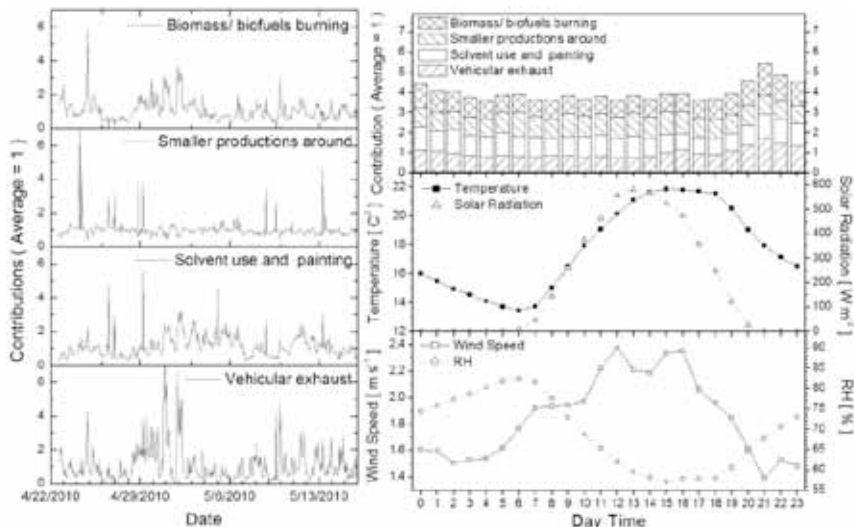

Figure 1: Identified time series plots (left), and diurnal patterns of source contributions estimated by PMF and meteorological parameters (right)

Combustion of waste of different origins could be a source of many compounds that were common to all factors. The average diurnal patterns of source contributions estimated by PMF are shown in Figure 1 (right). Total VOCs concentrations were higher during the day than at night since the most sources are related to anthropogenic activities. The average wind speed during the measurement period was higher at midday and thus caused stronger ventilation. Temperature

inversions near the ground occur mostly during night time inhibiting the vertical dilution of pollutants, causing elevated VOCs concentrations during the night. Daily minimum matches the most intense UV radiation and can be explained by photochemical destruction and OH-initiated oxidation of most VOCs. It can also be associated with stronger ventilation, as well as with dominant wind direction (NW) from rural environment during measuring episode. Above all, anthropogenic VOCs with small rate constants with NO_3 accumulate during the night.The factor related to traffic showed morning and afternoon rush hour peaks. The part associated with biomass/biofuels combustion showed peaks in the morning 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. Compounds grouped in factor related to smaller production around the sampling site and the local solvent use had elevated concentrations during the day and in the evening reflecting human activity. Based on the VOCs data set, possible transport process over Belgrade was investigated. CWT plots for two factors, Figure 2, denote that the sampling site was under the influence of several possible source regions. The main source areas are in border countries and Central Europe.
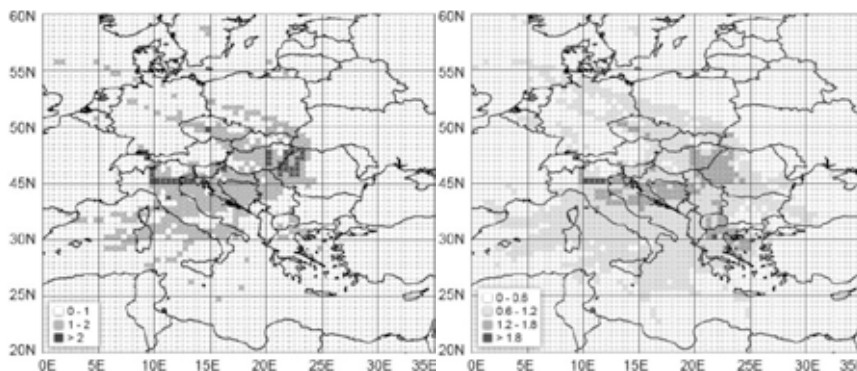
Figure 2: CWT (ppbv) maps for vehicular exhaust (left) and biomass/biofuels burning (right)

Acknowledgment

References

[1] W. Lindinger, A. Jordan and A. Hansel, Proton-transfer-reaction mass spectroscopy (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels, Chemical Society Reviews, 27,347 - 534, (1998).

[2] P. Paatero, The Multilinear Engine – A Table - Driven, Least Squares Program for Solving Multilinear Problems, Including the n - Way Parallel Factor Analysis Model. J Comput Graph Stat, 1,854 - 888, (1999).

[3] QY. Wang, YX. Zhang, R. Draxler, TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environmental Modeling & Software, 24, 938 - 939, (2008).

Coupling of in-mouth physical phenomena with nosespace analysis; a new method for understanding aroma release and perception from liquids

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Abstract

Results from coupling between an aroma release quantitative technique (PTR-TOF-MS) with an in-mouth imaging technique (B-Mode UltraSound Imaging) are presented in this work. This coupling was realized by triggering recording via external signal (5mV square pulse) that was measured by both apparatus and data postprocessing on this external trigger allowed synchronization of the time series to the precision (100 ms) of the least time-resolved signal (PTR-TOF-MS, 10 Hz). Using this unprecedented approach we are able to better understand the dynamics of aroma perception during food consumption before swallowing (i.e. during food manipulation in-mouth) and after swallowing. Orange juice was used as a case study to demonstrate the use of this new coupling and limonene/ethanol were monitored as a reference volatile markers. Due to its high volatility a sharp peak in the limonene trace is recorded by PTR-TOF-MS during each breath cycle, which can be well captured thanks to the high temporal resolution of the PTR-TOF-MS. This is mostly true for the exhalation first following swallowing and delay to the swallowing event can be used to evaluate how rapidly limonene is transported to the olfactory receptors. Beyond this case study, this method could offer new insights on how structured product destructuring in-mouth modifies perception based on simultaneous analysis of in-mouth manipulation and aroma release.

Introduction

To appreciate food or drink, mechanism of food oral processing are essential to understand how the consumption of food inside the mouse involves many operations including the first contact in mouth, bite, chewing, mastication. During these steps, food is destructured, mixed with saliva to form a cohesive ball (bolus).

Then during the swallowing of the food bolus or a sip of a drink, the food is pushing back through the mouse mainly by the tongue with a front-to-back squeezing action to enter the upper throat area, enter the esophagus to finish into the stomach by a squeezing action of the throat muscle.

During all these steps, aroma can release from food and can be transported from the oral cavity, or the throat or the esophagus to the olfactory receptors into the nose during exhalation. Amount of volatile released depend naturally of the absolute amount and physico-chemical properties of food and flavour compounds but also of the complex mechanism of food processing and transformation in mouth as well as the mouth physiology of the consumer.

Observation of the eating and drinking process has been realized by A. Buettner et al. [1] using Videofluoroscopy and Real-time Magnetic Resonance Imaging. This study shows how the tongue, pharynx and the soft palate are involved in mastication and swallow processes.

For the first time we propose a coupling of an real time imaging technique, the UltraSound instrument with the PTR-TOF-MS, a technology allowing to follow in real time aroma release from food during consumption.

Experimental Methods

Products used

A commercial orange juice (Eckes-Granini Group GmbH, Nieder-Olm, Germany) was chosen due to the high content of volatile terpenes in orange juice and strong volatile signal obtained by nosespace analysis. Two major compounds were followed and tentatively identified at m/z 47.0494, $(C_2H_6O)H^+$ corresponding mainly to ethanol and m/z 137.1325 corresponding mainly to limonene. These identifications were confirmed by an off-line measurement using static headspace GC-MS.

In vivo aroma release

Assessor exhaled air was sampled via two glass tubes inserted into the nostril and fixed on laboratory glasses [2]. This tailor-made nosepiece allow to breath comfortably during eating or drinking. The majority of the breath-air was released into the room. Only 80ml/min was drawn into the PTR-TOF-MS (Ionicon, Austria) via its transfer line connected to the nosepiece. To avoid condensation, the transfer line was heated at 100°C. A $^1/_8$ inch copper tubing of 20cm length was inserted inside the PTR-TOF-MS transfer line and around its $^1/_{16}$ inch inlet capillary peek tubing passing the heated transfer line. Due to the high copper thermal conductivity it was possible to heat the capillary peek tubing until its extremity.

The PTR-TOF-MS was set-up to monitor a full spectrum from m/z 10 to 350 every 0.1s. Internal mass scale calibration was done on a parasitic ion always present, m/z 29.9974$(NO)^+$ and acetone coming from usual air lab contamination and, as body metabolite, also present in breath air at m/z 59.0491 $(C_3H_6O)H^+$.

Assessor breathing pattern were also followed on m/z 59.0491 $(C_3H_6O)H^+$ corresponding to acetone.
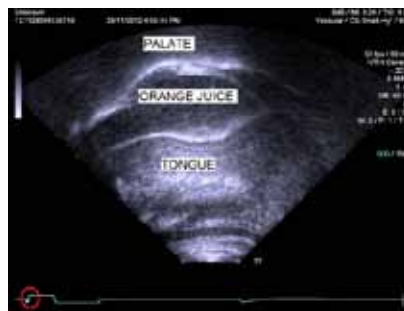
(a)   **(b)**

Figure 1: (a) Experimental setup: ultrasonic probe is maintain under the oral cavity to follow the process of drinking while the PTR-TOF-MS sample volatiles exhaled breath by breath. (b) Typical sagittal view recorded using the ultrasound. The circle marks the 5mV trigger recorded using the ECG input

In vivo oral processing

UltraSound imaging was acquired using a Siemens SC2000 (Siemens, Renens, Switzerland) used in parallel to observe in real time the drinking process by maintaining the ultrasonic probe under the oral cavity as shown Figure 1.

To synchronize precisely the acquisition time of the PTR-TOF-MS and the UltraSound instrument, a 5mV trigger (amplified to 1.6V for the PTR-TOF-MS) was recorded on analog input of both instruments (analogue input in PTR-TOF-MS and ElectroCardioGraphy input for the Ultrasound).

Results

Using this setup, we were able to identify and how each step of the swallowing influences aroma release. In Figure 2, one can see that three events *(first contact in mouth, swallowing start, swallowing end, all materialized by thick vertical lines)* were identified using the ultrasound images. First the product inlet in the mouth was recorded around 2.5s after the beginning of the experiment as normalized using the two equipments. The first peak of limonene was then measured 2.85s after the first contact of the product in mouth. We can see that limonene (m/z 137.1325) quickly rarefies in the nose space prior to swallowing, whilst ethanol (m/z 47.0491) sustains its intensity over two breath cycles prior swallowing. The initiation of swallowing and completion of swallowing are very close to one another ($\Delta t=0.2s$) and result in no aroma released during the swallowing phase itself. 1.29s after the completion of the swallowing phase, a new burst of limonene can be measured, which again quickly rarefies whilst ethanol rarefaction in the nose space is much slower. This period of 1.29s of delay between the two signals gives us a first approximation of the time spent by the volatiles in the pharynx before exhalation.
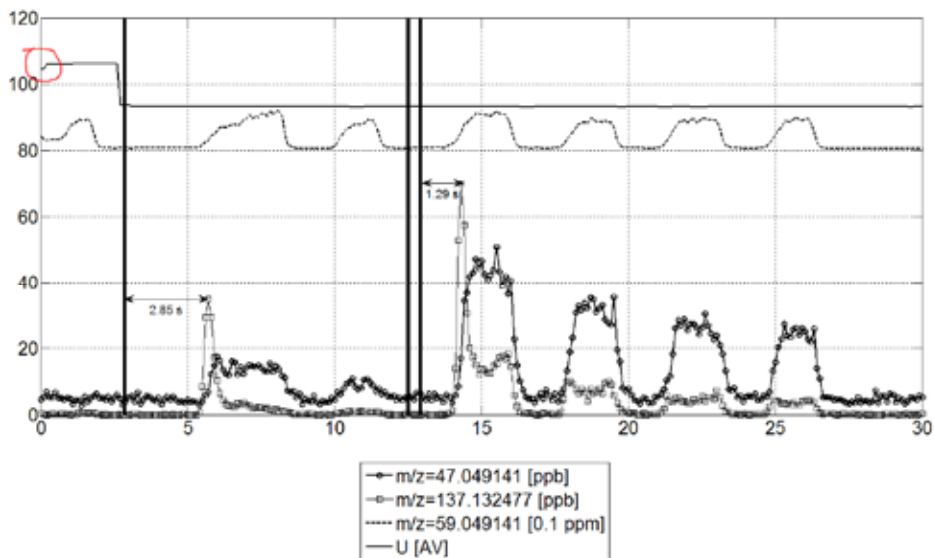

Figure 2: Typical results obtained from the coupling of aroma release measured using PTR-TOF-MS with the different phase of oral processing (see text for description). The circle marks the 5mV trigger recorded using the analogue input

Discussion

In this work, we report the first time resolved coupling between an in vivo aroma release and an in vivo imaging technique. Using this coupling we are able to comment quantitatively the effect of oral processing on aroma release and thus to understand the different phases of perception. Most interesting is the differences between the two volatiles tracked by PTR-TOF-MS. Limonene shows a very sharp initial peak which indicates that although a large container of limonene is present in the oral cavity, its concentration is not renewed in the nosespace.

Two mechanisms can be envisioned to explain this experimental behaviour; (i) the mass transfer of limonene to the headspace is limited by internal mass transfers within the orange juice, thus creating a gradient of limonene in the liquid bolus ($Bi \gg 1$) or (ii) during first contact in mouth and swallowing, headspace ethanol partitions within the mucus layer and is gradually release into the nosespace over several breath cycles. Given the low viscosity and little air flow occurring in the closed oral cavity, (i) seems unlikely, whilst (ii) would confirm the theoretical work of Doyenette et al. [3], which modeled mass transfer from the pharynx mucosa into headspace for a range of saliva viscosities and mucous layer thicknesses.

References

[1] Andrea Buettner, Ambros Beer, Christian Hannig and Marcus Settles, Observation of the swallowing process by application of videofluoroscopy and real-time magnetic resonance imaging-consequences for retronasal aroma stimulation, Chem. Senses, 26, 1211-1219, (2001).

[2] Santo Ali, Philippe Pollien, Christian Lindinger and Chahan Yeretzian, *in vivo* analysis of aroma release while eating food: a novel set-up for monitoring on-line nosespace air, 1st International Conference on Proton Transfer Reaction Mass Spectrometry and Its Applications, 161-164, (2003).

[3] Marion Doyennette, Clément de Loubens, Isabelle Déléris, Isabelle. Souchon, Cristian Trelea, A biomechanical model of swallowing for understanding the influence of saliva and food bolus viscosity on flavor release, Food Chemistry, 280, 1, 180-188, (2011).

Rapid Characterization of Dry-Cured Ham Volatile Compound Profile by PTR-Tof-MS: Effect of Geographical Origin, Rearing System and Cross-Breeding

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Abstract

Dry-cured ham is a valuable traditional foodstuff highly appreciated by consumers due to its unique flavour characteristics that depend on ripening conditions [1] and raw meat characteristics, i.e. animal age and genotype and type of feed during the fattening period [2, 3].

In this study we consider the effect of three different factors which can affect the final volatile profile of dry-cured hams: the geographical origin, and so the characteristics of the protected designation of origin (PDOs); the rearing system of the pigs, and the cross-breeding.

The effect of the geographical origin was researched using dry-cured hams from 4 PDOs: Italian PDOs *Prosciutto di Parma* (26 hams), *Porsciutto di San Daniele* (25 hams) and *Prosciutto Toscano* (29 hams), and the Spanish Iberian dry-cured ham PDO *Dehesa de Extremadura* (20 hams). The effect of the rearing system of the pigs on the final volatile profile of the dry-cured hams was investigated using the 20 Iberian dry-cured hams from the *Dehesa de Extremadura* PDO, 10 from pigs fattened outdoors on concentrated feed (*Campo*) and 10 from pigs fattened outdoors on acorn and pasture (*Montanera*) [4]. At last, the effect of the cross-breeding of the pigs was studied using the dry-cured hams from the Italian PDOs, which were produced from two different industrial cross-breeding pigs, a reference industrial hybrid (Italian Large White x Italian Landrace) and a Goland hybrid from the Italian Breeders Association. The hams were obtained and processed as fully described in Sánchez del Pulgar et al [5, 6]. From each ham a piece of the *Biceps femoris* muscle was taken, and 3 meat cubes of 1cm^3 (3 replicates) were prepared. The cubes were introduced into 40ml vials and equilibrated at 37°C for 30 min in a water bath prior to analysis.

Measurements were carried out using a commercial PTR-ToF-MS 8000 apparatus by direct injection of the head space mixture into the PTR-ToF-MS drift tube via a heated (110°C) peek inlet for 30s, taking 30 average spectra. Internal calibration of ToF spectra was performed off-line [7]. Peak detection and area extraction were performed according to the procedure described in Cappellin et al [8]. Principal components analysis (PCA) and Penalized

Discriminant Analysis (PDA) [9] were performed. To evaluate the results of the classification method we used a leave-group-out (LGO) method.

The rapid analysis of the headspace of the dry-cured hams by PTR-ToF-MS resulted in more than 600 mass peaks, and these data were used to perform the above mentioned analysis. Both the PCA and the PDA allowed a good separation of the dry-cured ham samples from different PDOs [5], probably due to the differences in the PDOs requirements, such as pig's breed (hybrid pigs from various crossing breeds such as Large Withe, Landrace and Duroc-Jersey in Italian PDOs, only Iberian pigs or their direct crossbreeds with Duroc-Jersey for Spanish Iberian hams [10]), salting process (use of small amounts of nitrates and nitrites allowed or banned) and ripening duration (12 months for Italian PDOs and at least 18 months for Iberian dry-cured ham PDOs). The statistical analyses allowed also the separation of the dry-cured Iberian ham samples from pigs fattened on different diets [6]. Nevertheless, it was not possible the discrimination of the dry-cured hams of the Italian PDOs according to the cross-breeding of the pigs, which indicates that this factor has a little effect on the final volatile profile of the dry-cured ham, much lower than other factors as the fattening diet of the pigs and the ripening conditions of the hams [2, 10].

Therefore, the geographical origin or the PDO (and so the ripening conditions and its duration) has a stronger effect on the final volatile profile of dry-cured hams than the fattening diet of the pigs, while the effect of the industrial cross-breeding seems to be negligible.

References

[1] J. Ruiz, J. Ventanas, R. Cava, A. Andrés and C. García. Volatile compounds of dry-cured Iberian ham as affected by the length of the curing process. Meat Science, 52, 19-27 (1999).

[2] A.I. Carrapiso, F. Bonilla and C. García. Effect of crossbreeding and rearing system on sensory characteristics of Iberian ham. Meat Science, 65, 623-629 (2003).

[3] T. Pérez-Palacios, T. Antequera, M.L. Durán, A. Caro, P.G. Rodríguez and J. Ruiz. MRI-based analysis, lipid composition and sensory traits for studying Iberian dry-cured hams from pigs fed with different diets. Food Research International, 43, 248-254 (2010).

[4] Real Decreto 1469/2007, de 2 de noviembre, por el que se aprueba la norma de calidad para la carne, el jamón, la paleta y la caña de lomo ibéricos. B.O.E. n. 264, November 3rd 2007, 45087-45104.

[5] J. Sánchez del Pulgar, C. Soukoulis, F. Biasioli, L. Cappellin, C. García, F. Gasperi, P. Granitto, T.D. Märk, E.; Piasentier and E. Schuhfried. Rapid characterization of dry cured ham produced following different PDOs by proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS). Talanta, 85, 386-383 (2011).

[6] J. Sánchez del Pulgar, C. Soukoulis, A.I. Carrapiso, , L. Cappellin, P. Granitto, E. Aprea, A. Romano, F. Gasperi and F. Biasioli. Effect of the pig rearing system on the final volatile profile of Iberian dry-cured ham as detected by PTR-ToF-MS.

[7] L. Cappellin, F. Biasioli, A. Fabris, E. Schuhfried, C. Soukoulis and T.D. Märk. Improved mass accuracy in PTR-TOF-MS: Another step towards better compound identification in PTR-MS. International Journal of Mass Spectrometry, 209, 60-63. (2010).

[8] L. Cappellin, F. Biasioli, P. Granitto, E. Schuhfried, C. Soukoulis, F. Costa and T.D. Märk. On data analysis in PTR-TOF-MS: From raw spectra to data mining. Sensors and Actuators B-Chemical 155, 183-190 (2011).

[9] P. Granitto, F. Biasioli, E. Aprea, D. Mott, C. Furlanello, T.; Märk and F. Gasperi. Rapid and non-destructive identification of strawberry cultivars by direct PTR-MS headspace analysis and data mining techniques. Sensors and Actuators B-Chemical, 121, 379-385 (2007).

[10] A.I. Carrapiso, A. Jurado and C. García. Effect of crossbreeding and rearing system on Iberian ham volatile compounds. Food Science and Technology International, 9, 421-426 (2003).

Product Analysis in Ethylene Ozonolysis by Chemical Ionization Mass Spectrometry

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Abstract

Product analysis in ethylene ozonolysis was performed using negative ion chemical ionization mass spectrometer (NI-CIMS) and proton transfer reaction mass spectrometer (PTR-MS). In the PTR-MS measurements, products of ethylene ozonolysis such as formaldehyde and formic acid were quantitatively measured. In the NI-CIMS measurements, hydroperoxides including the oligomers consisting of Criegee intermediates as a chain unit were observed. The results indicate that the Criegee intermediates play a critical role in the SOA formation from the ethylene ozonolysis.

Introduction

Atmospheric aerosols have effects on the human health, climate and visibility, and they also take part in heterogeneous reactions to affect the atmospheric chemistry.[1] While accurate atmospheric models are required to assess the true impact of atmospheric aerosols, current atmospheric models include significant uncertainties. One reason is because there is a lack of knowledge of formation mechanisms of SOA from ozonolysis of unsaturated organic compounds.

In this study, the reaction of ethylene with ozone was investigated as the simplest case of alkene ozonolysis, in order to promote understanding of atmospheric SOA formation mechanisms via reactions of unsaturated hydrocarbons and ozone.

Experimental Methods

Experiments were done using a 1 m^3 Teflon bag. Figure 1 shows the experimental setup. Synthetic air, ethylene (C_2H_4) and ozone (O_3) were introduced into the Teflon bag to start the reaction. A low pressure Hg lamp was used to produce O_3 by the UV irradiation at 185 nm of synthetic air. Flow rates were controlled using mass flow controllers. Experiments were done typically at room temperature and in atmospheric pressure with initial total volume of 0.85 m^3.

Gas phase species were measured by an ozone monitor, a negative ion chemical ionization mass spectrometer (NI-CIMS, and details are described below) and a proton transfer reaction mass spectrometer (PTR-MS, IONICON Analytic, Austria). Aerosol size distribution was measured by a scanning mobility particle sizer (SMPS, DMA model 3080, CPC model 3775, TSI Inc., USA). In the componential analysis of particles, particles were collected on the filter, then the filter was heated and vaporized compositions were measured by a NI-CIMS and a PTR-MS. Cyclohexane (c-hexane) was added as an OH scavenger to remove effects of OH radicals which are by-

products of the ethylene-ozone reaction. In a part of the experiments, methanol was added as a Criegee scavenger.
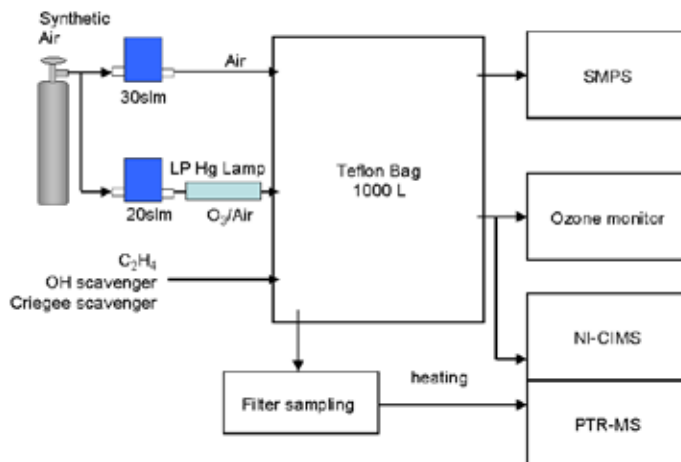

Figure 1: Schematic diagram of the experimental setup

Negative ion chemical ionization mass spectrometer (NI-CIMS)

A schematic diagram of NI-CIMS is shown in Fig.2. The NI-CIMS instrument consists of three regions: ion source region, chemical ionization region, and mass analysis region. At the top of the ion source, Cl^- was generated by the electron impact on the CH_3Cl/Ar gas mixture. Then, Cl^- was attached to SO_2, which was introduced via a side port of the ion source region, to produce the reagent ion for the chemical ionization, SO_2Cl^-, in the presence of Ar as the third body. The flow of the reagent ion entered the chemical ionization region and was mixed with the gas flow extracted from the Teflon bag. Product species such as carboxylic acids were ionized via the following reaction:

$$A + SO_2Cl^- \rightarrow A \cdot Cl^- + SO_2 \tag{1}$$
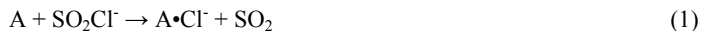
After the chemical ionization, ions including the product ions and unreacted SO_2Cl^- were introduced into the mass analysis region, where the ions were mass-analyzed by the quadrupole mass filter and detected by the secondary electron multiplier. Ion signals at a certain mass-to-charge ratio (m/z) were recorded as the count rate (counts per second, cps). The signal intensity of $A \cdot Cl^-$ normalized by SO_2Cl^- is proportional to the concentration of A. Hence, the count rates recorded by the mass spectrometer give the concentrations of A. Since the species, A, is detected as $A \cdot Cl^-$ through the reaction (1), subtraction of the mass number of chlorine (35 or 37) from the detected m/z will provide the molecular weight (MW) of A.

Figure 2: Schematic diagram of the NI-CIMS

Results and Discussion

The ethylene-ozone reaction was investigated with initial concentrations of 4.5 ppm O_3, 2.9 ppm C_2H_4, and 350 ppm c-hexane. SOA formation was observed by SMPS.

In the gas phase measurements by PTR-MS, ion signals assigned to HCHO (m/z = 31) and formic acid (m/z = 47) were observed. HCHO is primary product of ethylene ozonolysis. Formic acid is formed via isomerization of an excited Criegee intermediate, CH_2OO^*. Ion signals at m/z = 81 and 83 were observed and attributed to cyclohexanone and cyclohexanol, which are produced from the c-hexane + OH reaction.

In the gas phase measurements by NI-CIMS, ion signals assigned to products derived from the Criegee intermediate, CH_2OO, were detected. Figure 3 shows a typical mass spectrum obtained 2 hours after the initiation of the reaction as the black line. In this figure, normalized intensity is plotted against MW. The peaks at MW = 46 and 92 are assigned to be formic acid and hydroperoxymethyl formate (HPMF), respectively, the latter of which is produced from CH_2OO + formic acid. On the other hand, the peak at MW = 80 is assigned to be $HOOCH_2OOH$ produced from CH_2OO + H_2O_2. Additionally, peaks at MW = $46 \times n$ (n = 3, 4) and $80 + 46 \times n$ (n = 1, 2) were observed. They are assigned to be oligomeric hydroperoxides, which are produced from consecutive addition of CH_2OO units to HPMF or $HOOCH_2OOH$.

The oligomer group of MW = $46 \times n$ was observed also in the measurements of particle components. This indicates that the oligomer formation in the gas phase contributes to the SOA formation. In addition, other oligomers consisting of CH_2OO as a chain unit were observed in the particles, implying that the further oxidation processes occur in the particle phase.

To investigate the link between the CH_2OO oligomers and SOA formation, ethylene ozonolysis with 1300 ppm methanol as a CH_2OO scavenger was investigated. The SMPS measurements show that the SOA formation is strongly suppressed by adding methanol. Furthermore, NI-CIMS

measurements show that the signals of oligomers disappeared by adding methanol as shown in Fig. 3 by the gray line. These results strongly indicate that the oligomer formation involving CH_2OO plays a critical role in the SOA formation in the ethylene ozonolysis.
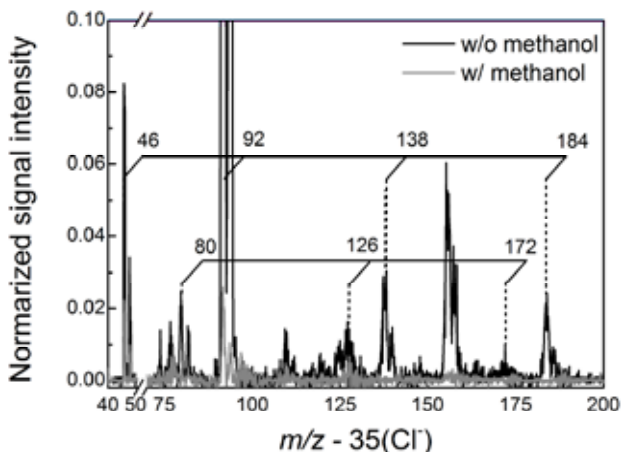

Figure 3: A typical spectrum by NI-CIMS in the gas phase measurements without (black line; $[O_3] = 4.5$ ppm, $[C_2H_4] = 2.9$ ppm and [c-hexane] = 350 ppm) and with a Criegee scavenger (gray line; [c-hexane] = 350 ppm and $[CH_3OH] = 1300$ ppm).

Summary

The SOA formation from ethylene-ozone reaction was investigated. Reaction products such as HCHO and formic acid were measured by PTR-MS. NI-CIMS detects hydroperoxides including CH_2OO oligomers both in the gas and aerosol phase, which indicates that the oligomer formation in the gas phase contributes to the SOA formation. Experiments with the addition of the Criegee scavengers show that CH_2OO plays a critical role in the SOA formation from the ethylene-ozone reaction. Further investigation of the oligomer formation from the Criegee intermediates will promote understanding of the atmospheric SOA formation mechanisms via reactions of unsaturated hydrocarbons and ozone.

Acknowledgement

References

[1] J. H. Kroll and J. H. Seinfeld, Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmospheric Environment 42, 3593-3624, (2008).

Use of PTR-MS online monitoring for validation of emission test chamber experiments: Reference source and odor assessment

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Abstract

Continuous determination of volatile organic compounds gained increased importance in the field of indoor air quality since short-term emission events need to be assessed. This paper shows two exemplary applications. First, the development of reference sources for the validation of emission test chamber measurements is often connected to non-steady-state measurements with rapid changes in the chamber air concentration. The testing of these new sources needs high-time resolved measurements that are advantageous compared to thermal desorption methods. Second, the sensory evaluation of products using emission test chambers gains importance due to changes in certification regulations. The time-related performance of odor standards in olfactometers can be assessed via PTR-MS even at comparatively large concentrations.

Introduction

In order to maintain a healthy indoor air quality, permanent regulatory efforts are performed to minimize the release of organic compounds in the indoor environment. Regulation demands emission tests to be performed under well controlled environmental conditions which require emission cells or emission test chambers in most cases. The poster exemplarily describes two PTR-MS applications within recent and important fields of indoor air quality research: a) reference material development and b) sensory evaluation of consumer/building products.

One of the most important aspects in emission test chamber measurements is process validation. While chemical analytics may be validated easily, the test procedure needs a reference sample that can be reproduced identically for round-robbin tests. Possible approaches range from liquid reservoirs with known diffusion hindrance [1] to polymer materials with a precisely known initial concentration of the target compound [2]. The release pattern of the latter reference source follows a rapid kinetic that can be predicted by feasible diffusion/emission models. However, the validation of this source type needs a high-time resolved analytics because the system does not reach steady-state conditions. The PTR-MS has proven to be advantageous compared to discontinuous thermal desorption methods to estimate differences between predicted air concentration and measured air concentration.

Another topic of high interest in the field of indoor air quality is the regulative determination of the odor of consumer products and building products. The sensory evaluation of building products gained importance since publication of ISO 16000-28, which describes procedures for the odor assessment of indoor products via emission test chamber measurements coupled with olfactometry [3]. Modern olfactometers provide odorant pulses that need to feature rapid steady-state conditions. The performance of a commercial olfactometer using PTR-MS technique has been reported in 2010 [4]. In the framework of a round-robbin test, WKI built a reference standard according to ISO 16000-28 and determined the performance via PTR-MS.

Experimental Methods

The reference material was provided by NIST in the framework of an international round-robbin test. The complete data set and details on the material are published elsewhere [2]. The present samples comprises of four small plastic sheets (6 cm x 6 cm x 0.025 cm) which were tested in 2 sets in a 0.25 m³ stainless-steel emission test chamber. Both sets of reference materials were measured subsequent in the same chamber. The sheets were placed in a special holder provided by NIST. The emission test chamber was operated at 23°C, 50% r.h. and an air exchange rate of 1.2 h^{-1}. Air samples were collected on Tenax TA filled tubes after 24 h, 48 h and 72 h in duplicate (150 mL/min, 40 min). Additional samples that aim at the maximum toluene concentration were also collected within the first 3 h after loading. The hs-PTR-QMS (Ionicon Analytik) continuously recorded the toluene concentration via m/z 93.

The odor reference has been designed to provide five selectable acetone concentrations in an air stream of constant temperature and humidity. A specially designed saturation units was developed to reach a stable concentration rapidly. The hs-PTR-QMS has been used to determine the time profile of the odorant pulses via m/z 59.
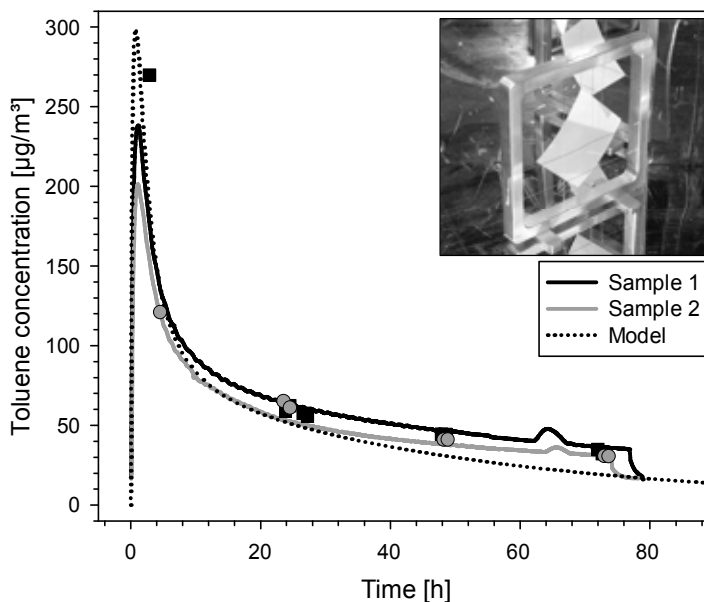
Figure 1: Comparison between predicted toluene concentration and measured concentration via PTR-MS (solid line) and TD-GC/MS analysis (symbols) for both reference material samples. The two sample sheets and the aluminum holders in the emission test chamber are shown in the insert.

Results and Discussion

The development of the toluene concentration could be recorded for the chamber experiment at high time resolution. Within the first 10 hours after loading of the chamber the model predicts a peak chamber air concentration of toluene in the range of 300 μg/m³. After 20 h the concentration is expected to drop below 50 μg/m³. In case of both sets of samples the measured peak concentration is lower while the time to drop below 50 μg/m³ has been underestimated (see Figure 1). The discontinuous thermal desorption measurements are in good agreement with the results of the PTR-MS but show increasing deviations near the peak concentration. This complies to the expected uncertainties of the accumulating thermal desorption technique and rapidly fluctuating air concentrations. Between 60 h and 80 h a short-term increase in the toluene concentration was recorded by the PTR-MS. This increase was caused by a heating source near the emission test chamber that accidently increased the temperature in the chamber for < 5 h. After removing the heating source, the concentration development follows the initial decay pattern. This increase could not be observed via the discontinuous analytics.
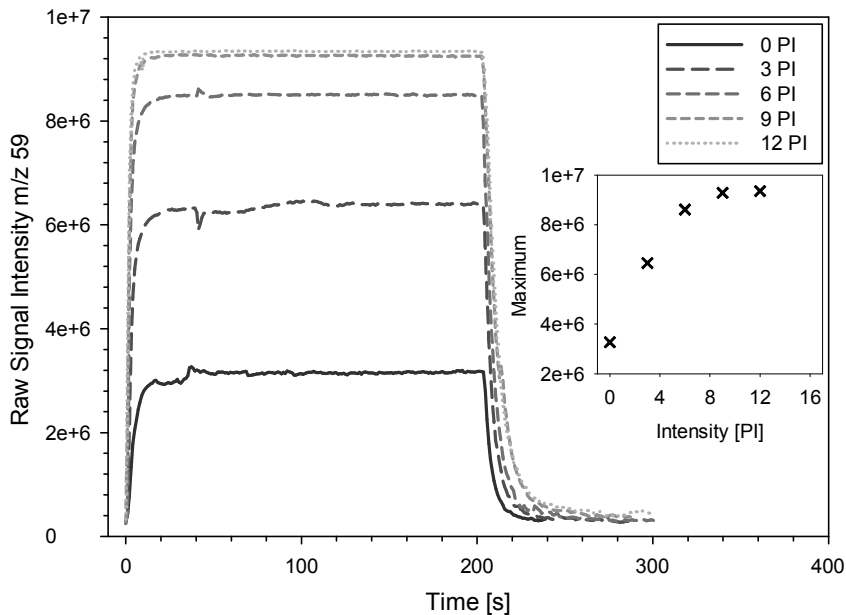
Figure 2: Time profile of acetone pulses from the odor reference at different target intensities. The dependence between steady-state signal and odor intensity is given in the insert. (The unit of the odor intensity is PI, perceived intensity.)

The characterization of the odorant pulses from the reference olfactometer revealed that the time to reach steady-state conditions did not depend on the target intensity of the system (see Figure 2). Even at the highest applied acetone concentration (12 PI, ~100 ppm) the time to reach steady-state was ~10 s. After that, the air concentration was stable (< 1 % fluctuation) and showed no depletion of the saturation source even at the highest acetone inflow. Building products are

usually evaluated in the odor range between 0 PI and 15 PI (perceived intensity) [5] which corresponds to a concentration range of 8 ppm to 124 ppm. Within the range above 8 PI the PTR-MS detector is not linear and reaches saturation (see insert in Figure 2). Even though the PTR-MS is not designed for measuring these large concentrations the time profile – time to reach steady-state and stability of the odorant pulse - can be determined with good precision. Quantitative determination of the odor steady-state concentrations needs dilution techniques which might increase the uncertainty of the measurement.

References

[1] W.J. Wei, Y.P. Zhang, J.Y. Xiong, M. Li, A standard reference for chamber testing of material VOC emissions: Design principle and performance, Atmospheric Environment 47, 381-388, (2012).

[2] C. Howard-Reed, Z. Liu, J. Benning, S. Cox, D. Samarov, D. Leber, A.T. Hodgson, S. Mason, D. Won, J.C. Little, Diffusion-controlled reference material for volatile organic compound emissions testing: Pilot inter-laboratory study, Building and Environment 46, 1504-1511, (2011).

[3] ISO 16000-28, Indoor air - Part 28: Determination of odour emissions from building products using test chambers (draft) (2010), Beuth-Verlag, Berlin.

[4] J. Beauchamp, J. Frasnelli, A. Buettner, M. Scheibe, A. Hansel, T. Hummel, Characterization of an olfactometer by proton-transfer-reaction mass spectrometry, Measurement Science and Technology 21, 025801, (2010).

[5] W. Horn, J. Kasche, O. Jann, D. Muller, W. Plehn, Intensity of odour and emissions from building products - Conception of the procedure and interlaboratory comparison, Gefahrstoffe Reinhaltung Der Luft 67, 71-75, (2007).

In vivo aroma release by APCI-MS and PTR-MS: impact of water content of exhaled air and evidence for competition between aroma compounds.

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Abstract

Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) or proton transfer reaction mass spectrometry (PTR-MS) has been in use frequently for *in vivo* aroma release studies [1–3]. In APCI-MS, protonated water clusters formed from moisture in the expired air are used as reagent ions. Yet the influence of a change in relative water content in the ionization gas on the data collected have been rarely studied and conflicting results were obtained [4 & 5]. **In this context our first objective was to study the impact of water content of the expired air on the level of aroma release measured by APCI-MS and to compare with the results obtained by PTR-MS.** Otherwise, Le Quéré et al. [6] showed *in vitro* a competition between aroma compounds whatever the ionization method used (APCI or PTR). This competition could be influenced by the chemical characteristics of aroma compounds and their respective amount in the mixture [7]. **In this context our second objective was to check *in vivo* the reality of this competition phenomenon.**

In a first experiment, 12 subjects with various levels of water in the expired air were selected. Aroma release during consumption of fresh cottage cheese flavoured with ethyl propanoate (EP) at 25 ppm or nonan-2-one (NO) at 8 ppm or a mixture of these two compounds was followed by APCI-MS and PTR-MS. Results showed no significant correlation between detection level and quantity of aroma release and the water content of expired air whatever the MS-method used.

In a second experiment, aroma release of twelve subjects was followed by APCI- and PTR-MS during their consumption of eight fresh cottage cheeses flavoured either with EP at 0, 10 or 20 ppm or by NO at 0, 4 or 10 ppm and all possible binary mixtures. Confirming previous studies obtained *in vitro* [6 & 7], our results showed a competition between the two aroma compounds studied whatever the MS-method used (APCI-MS or PTR-MS).

Introduction

Breath-by-breath measurements by mass spectrometry, applying techniques such as atmospheric pressure chemical ionization mass spectrometry (APCI-MS) or proton transfer reaction mass spectrometry (PTR-MS) have been in use for a few years as a fairly common methodology for *in vivo* aroma release studies [1–3]. In APCI-MS, protonated water clusters formed from moisture in the expired air are used as reagent ions. Yet few studies have examined the influence of a change in relative water content in the ionization gas on the data collected. In addition, these studies present contradictory results. Thus, Sunner et al. [4] reported a decrease of APCI-MS sensitivity when the relative humidity increased while Zehentbauer et al. [5] showed that moisture enhancement decreased molecules fragmentation and increased sensitivity of APCI-MS. **In this context our first objective was to study the impact of water content of the expired air on the level of aroma release measured by APCI-MS and to compare with the results obtained by**

PTR-MS. Otherwise, Le Quéré et al. [6] showed *in vitro* a competition between aroma compounds whatever the ionization method used (APCI or PTR). This competition could be influenced by the chemical characteristics of aroma compounds and their respective amount in the mixture [7]. **In this context our second objective was to verify *in vivo* the reality of this competition phenomenon.**

Experimental Methods

Subjects: Twelve subjects were selected on the various water content of their expired air (from 66.2 ± 0.9 % to 79.7 ± 7.8 %, means 72.6 ± 4.0 %).

Experiment 1

Humidity Sensor: Water content in the expired air was determined using humidity sensor (SHT11, Sensirion, Staefa, CH). This sensor was inserted into a plastic tube ended with a glass nose piece. Water content was averaged over 100 seconds.

Products: Fresh cottage cheese (40 % fat content on dry matter) flavoured with 25 ppm of ethyl propanoate (EP) or 8 ppm of nonan-2-one (NO) was consumed by the subjects.

Aroma release measurement: Aroma release was followed using both techniques, atmospheric pressure chemical ionization – mass spectrometry (APCI-MS) and proton transfer mass spectrometry (PTR-MS). For APCI-MS measurements, air from the nose was sampled from one nostril at an average flow rate of 37 mL/min and introduced into a specially modified APCI source of an Esquire-LC ion trap mass spectrometer (Bruker Daltonique, Wissembourg, France) [6]. For PTR-MS measurements, expired air was introduced into a PTR-ToF-MS (PTR-ToF 8000, Ionicon Analytik, Innsbruck, Austria) at an average flow rate of 52 mL/min. The hydronium precursor ion was produced from distilled water vapor. The inlet and drift tube temperature was set at 80°C and drift tube pressure was kept between 2.2 and 2.4 mbar. Full scan mass spectra were recorded between *m/z* 2.79 and *m/z* 183.26 in 0.108 s. E/N ratio value was set at 117 Td. Both volatiles (EP and NO) were monitored according to their protonated molecular ion (MH^+).

Method: Three replicates per subjects and per cheese were performed in two sessions. In each session, water content of expired air was measured previously to the aroma release measurements. Then, the subject was asked to position a plastic tube in one nostril and to breathe normally. After an initial swallow, the subject was instructed to place a tea-spoon content (4 g) of flavoured fresh cottage cheese in his mouth and to keep it without swallowing for 20 s. The subject was then asked to swallow. Aroma release was recorded until no more flavour compound was detected.

Data analysis: Background corresponding to the expired air before placing the food into the mouth was firstly subtracted from each individual release curve of each aroma compound. Area under curve (AUC) representing the quantity of aroma release was then extracted. The link between the water content of expired air and the quantity of aroma release was studied by linear regression.

Experiment 2

Products: Eight fresh cottage cheeses (40 % fat content on dry matter) flavoured either with EP at 0, 10 or 20 ppm or with NO at 0, 4 or 10 ppm and all possible binary mixtures were consumed by the subjects.

Aroma release measurement: All the experiments were conducted with APCI-MS and with a PTR-Tof-MS instrument (see experiment 1).

Method: Three replicates per subjects, per cheese and MS method of aroma release measurement (APCI-MS and PTR-MS) were performed in two sessions. The session organization was the same as for experiment 1.

Data analysis: From background subtracted curve (see experiment 1) from each individual release curve of each aroma compound, area under curve (AUC) representing the quantity of aroma release was extracted. Two factors ANOVAs were performed (subjects, flavour compounds and subjects*flavour compound).

Results – Discussion

Experiment 1

An intra-individual variability of water content of the expired air has been observed (approximately 10 %). As shown on figure 1 for APCI-MS, no significant correlation has been shown between quantity of aroma compound detected and the water content of expired air, whatever the aroma compound studied. With PTR-MS same results were obtained (data not shown).
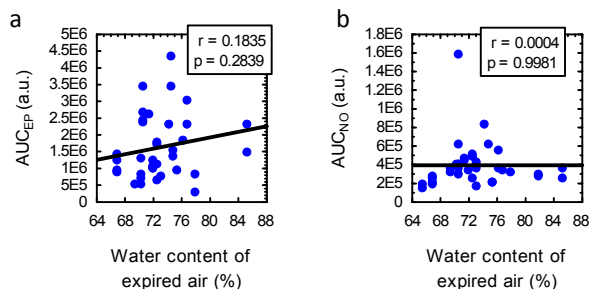
Figure 1: Correlation between area under curve (AUC) of ethyl propanoate (EP) release (a) and of nonan-2-one (NO) release (b) and water content of expired air, using APCI-MS).

We concluded that the reactivity of the ion plasma (H_3O^+) into the source was either not modified by the water content of expired air or modified but at a level that cannot explain the inter-individual variability observed in quantity of aroma release.

Experiment 2

Detection of EP at 10 ppm, is not significantly modified by the presence of NO whatever the two concentrations studied (NO 4 or 10 ppm) and the MS method used (APCI-MS: $F_{(2,72)}=0.07$; $p>0.05$ (Figure 2A) or PTR-MS: $F_{(2,70)}=1.38$ $p>0.05$ (Figure 2B)).
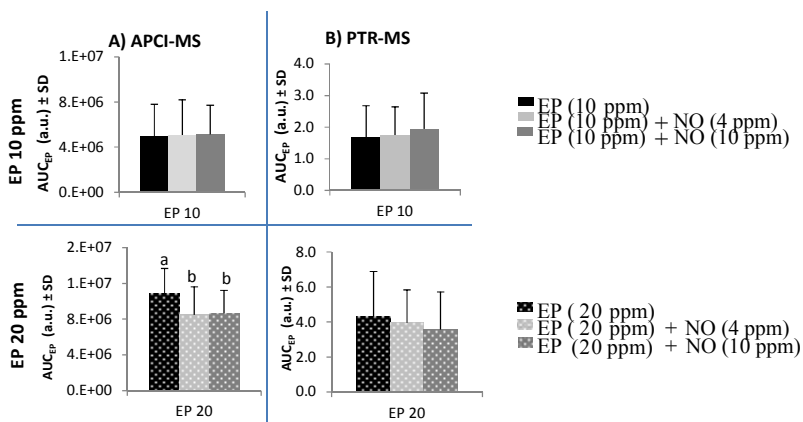
Figure 2: Influence of NO content on EP detection by APCI-MS (A) and by PTR-MS (B).

Detection of EP at 20 ppm, is significantly reduced by the presence of NO whatever the two concentrations studied with APCI-MS ($F_{(2,72)}=9.5$; $p<0.01$) (Figure 2A) but not with PTR-MS even though a tendency also exists ($F_{(2,70)}=2.86$; $p=0.06$) (Figure 2B).

With APCI-MS, detection of NO is significantly reduced by EP whatever the concentration of NO ($F_{(2,72)}=38$; $p<0.0001$ for NO 4 ppm and $F_{(2,72)}=4.3$; $p<0.05$) for NO 10 ppm) (Figure 3A), but the effect of EP is greater with NO at 4 ppm than with NO at 10 ppm. With PTR-MS, detection of NO at 4 ppm is significantly reduced by EP at 10 ppm but not by EP at 20 ppm ($F_{(2,70)}=11.3$ $p<0.05$) (Figure 3B). With 10 ppm of NO in the fresh cottage cheese, detection of NO is not modified by EP ($F_{(2,70)}=0.9$ $p>0.05$).
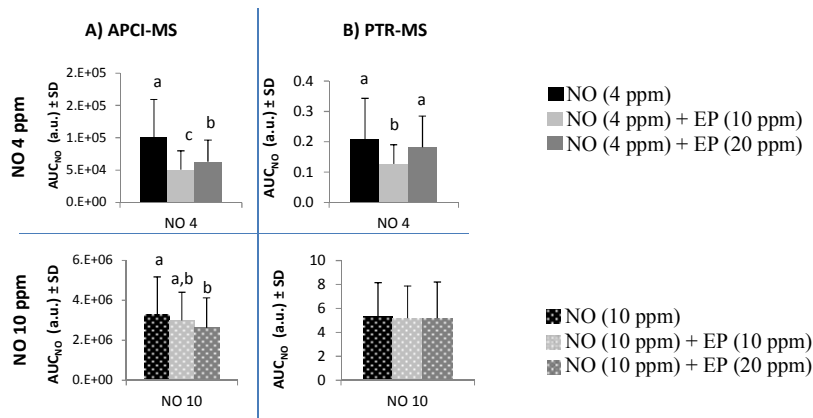
Figure 3: Influence of EP content on NO detection by APCI-MS (A) and by PTR-MS (B).

As observed by Buffo and Reineccius [7] in an *in vitro* study, our results show ionization competition between aroma compounds whatever the MS-method used, even if the competition seems to be greater with APCI-MS than with PTR-MS. This competition seems to be flavour compound and concentration dependent. Further studies would be necessary to clarify this competition phenomenon.

References

[1] Taylor, A.J.; Linforth, R.S.T. Techniques for measuring volatile release in vivo during consumption of food. Flavor Release; Roberts, D.D., Taylor, A.J., Eds.; American Chemical Society: Washington, DC; pp 8–21, (2000).

[2] Boland, A.B.; Delahunty, C.M.; van Ruth, S.M. Influence of the texture of gelatin gels and pectin gels on strawberry flavor release and perception. Food Chem., 96, 452–460, (2006).

[3] Weel, K.G.C.; Boelrijk, A.E.M.; Alting, A.C.; van Mil, P.J.J.M.; Burger, J.J.; Gruppen, H.; Voragen, A.G. J.; Smit, G. Flavor release and perception of flavored whey protein gels: Perception is determined by texture rather than by release. J. Agric. Food Chem., 50, 5149–5155, (2002).

[4] Sunner, J., Nicol, G. and Kebarle, P. Factors Determining Relative Sensitivity of Analytes in Positive Mode Atmospheric-Pressure Ionization Mass-Spectrometry. Anal.. Chem., 60(13), 1300-1307, (1988).

[5] Zehentbauer, G., Krick, T. and Reineccius, G. A. Use of Humidified Air in Optimizing APCI-MS Response in Breath Analysis. J. Agric. Food Chem., 48(11), 5389-5395, (2000).

[6] Le Quere, J.-L.; Gierczynski, I.; Langlois, D.; Semon, E. Nosespace with an ion trap mass spectrometer: quantitative aspects (Book Section). In Flavour Science: Recent Advances and Trends, Amsterdam (NLD) ed.; Bredie, W. L. P.; Petersen, M. A., Eds. Elsevier, Oxford (GBR). Vol. 43, pp 589-592, (2006).

[7] Buffo, A.; Reineccius, G.A. Determination of linear response in the detection of mixtures of aroma compounds by atmospheric pressure ionization-mass spectrometry (API-MS). Flavour and Fragrance Journal 23, 16-22, (2008).

In-vivo volatile organic compound (VOC) release from fresh-cut apple cultivars: PTR-Quad-MS and PTR-ToF-MS

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Abstract

Using a PTR-QUAD-MS it has previously been shown that soft apple cultivars release a higher concentration of volatile organic compounds (VOC) compared to firm apple cultivars. By analyzing in-vivo nose space data the cultivars could be discriminated based on their volatile release patterns. In general it was found that the diffusion of VOC within the nasal cavity was dependent on particle breakdown during mastication which was faster for soft apples and slower for firm apples. Considering the limitations of the PTR-QUAD-MS (slow data acquisition, lower temporal resolution and limited mass range), and a recent increase in interest in in-vivo studies, this study was further investigated using the recently commercialized PTR-ToF-MS instrument. These results obtained were in general in agreement with the PTR-QUAD-MS findings with the benefit of obtaining a dataset of higher resolution.

Introduction

The acceptability and recognition of apple quality arises from a complex set of sensory sensations associated with the perception of aroma, taste and texture. Interactions occurring between these different modalities impact upon their perception. Using a PTR-QUAD-MS we have previously shown that apple cultivars can be differentiated based on their in-vivo volatile organic release (VOC) patterns [1]. Firm apples such as Firm apples such as Granny Smith during in vivo nose space release had a flat sustained release due to the cohesive nature of the cells. In contrast, soft apples like Golden Delicious gave fast release followed by a rapid decay as the apple structure was rapidly broken down during consumption. Based on these results it was concluded diffusion of VOC within the nasal cavity was dependent on the rate and extent of particle breakdown during mastication. Granny Smith which contained low amounts of VOC as determined by headspace measurements, gave similar results during in-vivo, nose-space analysis. In contrast, soft apples such as Golden Delicious which contained high amounts of VOC and this was clearly shown in the in-vivo nose space results: diffusion of VOC within the nasal cavity was dependent on particle breakdown during mastication.

Due to the increasing interest in monitoring flavour compounds during food consumption and in investigating the relationship between flavor release and texture [2, 3] we initiated a study to further investigate VOC release from apples. Due to the known limitations of the PTR-QUAD-MS, the PTR-ToF-MS was chosen as the instrument of choice. The present study will outline the

differences between the two methods and how PTR-ToF-MS can increase the temporal resolution of nose space studies.

Experimental Methods

In-vivo nose space protocol

Apple sample size (ø 18 mm, length 20 mm) and experimental protocols were carried out under similar conditions of the previous study [1]. Six panelists (3 male and 3 female) participated in the analysis. Panelists were instructed to breath through a PTFE tube (ø 6 mm, length 50 mm) inserted into a heated (95°C) nosepiece (Ionicon Analytik GmbH, Innsbruck, Austria) connected to the PTR-ToF-MS 8000 inlet. Exhaled air was collected via the heated PEEK tube (110°C, 0.055") at a flow rate of 300 sccm. All measurements were carried out at 600V; drift temperature 110°C; drift pressure 2.25mbar for a corresponding E/N value of 140 Td (10^{-17} cm^{-2} V^{-1}s^{-1}).

After 30 s of normal breathing, each panelist was instructed to consume the apple sample by free mastication. The panellists were also asked to signal with their hand: the time of sample introduction; each swallowing event and the end of consumption. After that, the panellist was asked to continue to breath normally for a further 30 s before the nosepiece was removed.

In the case of PTR-QUAD-MS only few selected masses have been monitored [1] while for the ToF version complete spectra up to m/z 400 have been recorded every second. In the case of PTR-Quad-MS only 5 different cultivars have been measured [1] while in the case of PTR-ToF-MS we measured more than 20 cultivars over two years.

Data analysis

ToF spectra analysis was carried out in accordance to Cappellin and others (2011) [4]. Statistical packages used were developed using MATLAB (MathWorks, Natick, United States). Due to the mass amount of data collected from this technique, only two cultivars, Granny Smith and Golden Delicious will be explained. The mass ion corresponding to acetaldehyde (m/z 45; m/z 45.0333) was chosen due to its high volatile concentration during in-vivo analysis. Acquired spectral data were plotted as four period moving average trend lines with indicated swallowing events.

Results and Discussion

As an example, the nose space release profile for a selected compound and for one panelist is illustrated in Figures 1 and 2, where Figure 1 represents data from the PTR-QUAD-MS and Figure 2, data from the PTR-ToF-MS. To show a direct comparison, both figures were graphed using the same panelist and cultivars. Both figures show similar trends. Looking at the Area under the Curve, soft Golden Delicious contained a higher concentration of acetaldehyde in comparison to Granny Smith. With regards to mastication, the panelist took a longer time to consume the Granny Smith sample using 4 - 5 swallows in comparison to Golden Delicious (3 – 4). Similarities between the results from both techniques confirm that VOC release rates are influenced by both cultivar and texture.

Results obtained from the PTR-ToF-MS had smoother peaks giving the opportunity to study volatile compound release rates of different apple cultivars during in-vivo analysis. Swallowing events are clearer in Figure 2 where a swallowing event is always followed by an increase in volatile compound release. Overall, the use of a PTR-ToF-MS is beneficial when conducting in-vivo nose space studies. Further development of these findings including influences of panel variability on VOC release will be discussed in the poster.
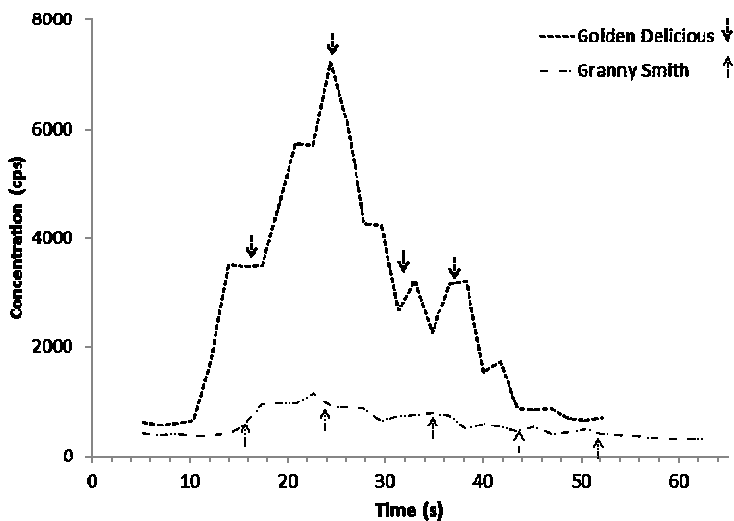
Figure 1: Nose space release profiles from the PTR-QUAD-MS of one panelist from two different apple cultivars for mass ion m/z 45 tentatively known as acetaldehyde. The arrows represent all swallowing events for each cultivar.
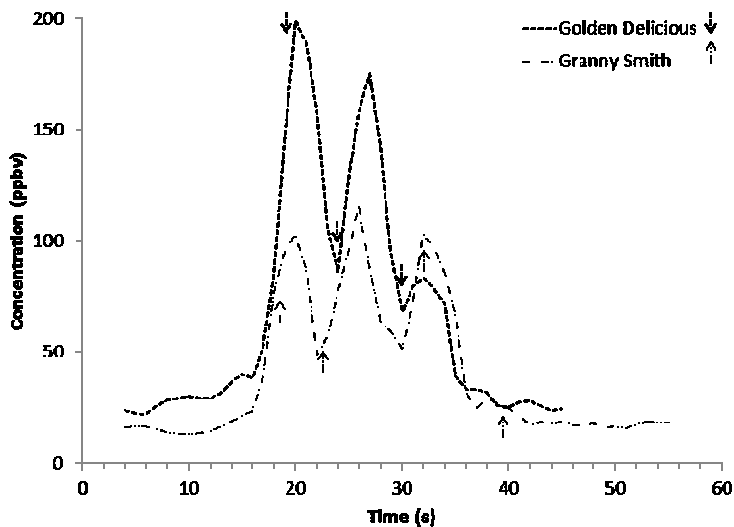

Figure 2: Nose space release profiles from the PTR-ToF-MS of one panelist from two different apple cultivars for mass ion m/z 45.0333 tentatively known as acetaldehyde. The arrows represent all swallowing events for each cultivar.

References

[1] V.J.L Ting, C. Soukoulis, P. Silcock, L. Cappellin, A. Romano, E. Aprea, P.J. Bremer, T. Märk, F. Gasperi, and F. Biasioli. In Vitro and In Vivo flavour release from intact and fresh-cut apple in relation with genetic, textural, and physicochemical parameters, Journal of Food Science 77, 1226 – 1233 (2012).

[2] F. Biasioli, C. Yeretzian, F. Gasperi, and T. Märk, PTR-MS monitoring of VOCs and BVOCs in food science and technology, Trends in Analytical Chemistry 30, 968-977, (2011).

[3] S. Heenan, C. Soukoulis, P. Silcock, A. Fabris, E. Aprea, L. Cappellin, T.D. Märk, F. Gasperi, and F. Biasioli. PTR-ToF-MS monitoring of in-vitro and in-vivo flavor release in cereal bars with varying sugar composition, Food Chemistry 131, 477-484, (2011).

[4] L. Cappellin, F. Biasioli, P. Granitto, E. Schufried, C. Soukoulis, F. Costa, T. Märk, and F. Gasperi, On data analysis in PTR-ToF-MS: from raw spectra to data mining, Sensors and Actuators B 155, 183-190 (2011).

Effect of background contaminations from the clinical environment on breath gas profiles

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Abstract

A crucial issue in breath research is the impact of environmental compounds on breath profiles. Among more than 1000 different compounds detected in human breath only few are known to be originating from endogenous sources. As most studies are performed in a clinical environment typical contaminations such as disinfectants, anesthetics or emission from plastic materials have to be taken into account. The aim of this study was to investigate the effect of exogenous contaminants from the clinical environment onto breath profiles of hospital staff.

15 physicians, 10 PACU nurses and 7 staff members not working in the OR/PACU. Exhaled breath of all participants was analyzed by means of PTR-TOF in the central PACU of the Rostock University Medical Center. Samples were collected before and after working shifts of the volunteers. In parallel, inspired and room air concentrations were determined.

Breath profiles from physicians and nurses showed distinct concentrations of anesthetics and disinfectants after the end of their shift. Breath profiles of the control group did also contain typical clinical contaminants. Depending on the daytime high concentrations of anesthetics and/or disinfectants were also detected in inspired air. Expired sevoflurane concentrations in physicians were 27 times higher at the end of their shift (in ppbV; Median: 210.83 ppb, 25th percentile: 118.23, 75th percentile: 329.56) compared to the beginning of their shift (7.82, 2.65 - 32.67). The control group showed a similar behavior (beginning: 202.02, 155.39 - 403.00; end: 9.27, 2.98 - 7.64), while expired concentrations of nurses depended on the time of their shift (early, late or night shift). However, inspired concentrations showed the same tendencies as expired concentrations. Inspired concentrations of physicians at the beginning of their shift e.g. were between 1.43 (25th percentile) and 15.24 (75th percentile) with a median of 2.65. At the end of their shift inspired concentrations were between 336.48 (25th percentile) and 1118.14 (75th percentile) with a median of 629.89. Substances concentrations of endogenous breath markers such as acetone did not show significant differences and inspired concentrations of these substances were low.

Chronic as well as acute contaminations from the clinical environment impacted onto breath profiles. Concentrations of typical clinical contaminants were found in orders of magnitudes higher than endogenous compounds. Simple subtraction of room air concentrations does not solve the problem of clinical background contamination but may help to distinguish between acute exposures and previous loads.

Automated Setup for High Precision Measurements of Henry Law Constants of Volatile Organic Compounds over a Large Temperature Range

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Abstract

An improved setup was developed to measure the liquid-air partition coefficients (Henry Law Constants, HLC) of volatile organic compounds (VOCs). The method is based on gas stripping a dilute solution of a volatile organic compound (VOC) and direct, time-resolved analysis by proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS). This approach bears the following advantages: (i) rapid, even for very low volatile compounds, (ii) applicable over a large temperature range (4°C to 85°C in the case of water as solvent) (iii) does not require a calibration or knowledge of the initial concentration of the solute, and has a very high temperature stability (ΔT better than $\pm$ 0.1°C). The setup is fully automated allowing continuous measurements of HLCs over a wide temperature range under well controlled conditions. The method was applied to measure the HLCs of over 20 molecules in water over a temperature range of 4°C to 85°C.

Introduction

The partitioning of volatile organic compounds (VOCs) between liquids and air is of significance to a large variety of scientific fields and phenomena. It governs critical phenomena in environmental and atmospheric chemistry, is essential to the partitioning of metabolites in living organism and to the aroma of food products [1-4]. Furthermore it is strongly temperature dependent. Until now, several studies on the temperature dependence of the air-water partitioning coefficients have been performed, but either have they been restricted to a small temperature interval, or the authors used a combination of methods to cover a greater temperature range, each of them optimized for a distinctive temperature interval or for a distinctive group of substance properties. Furthermore, results between different authors and methods often greatly vary.

The advantages of the dynamic and direct method for determining Henry's Law Constants (HLC) presented here lie in covering the complete temperature range, from below room temperature to the boiling point of water, using always the same unique experimental setup. Due to the new automated setup, results are highly reproducible. Depending on the volatility of the compounds, the measurement can be performed either relatively fast (several minutes) or can extend over days for the least volatile compounds (at least up to HLC = 14 mol·m^{-3}·Pa^{-1}) while ensuring high accuracy. Furthermore, the initial and absolute concentration of the analyte does not need to be known; only relative concentration need to be considered. These allow among others to include substances over a very large range of volatility and solubility. Here we discuss the critical details of the automated setup and present some selected results.

Experimental Methods

The experimental setup is shown in Figure 1. For measuring the HLC of a VOC, a highly diluted solution of the respective VOC in water was filled in cell 2 (100 ml, Figure 1c, right cell). Cell 1 (Figure 1c, left cell) was filled with distilled water (100 ml) in order to saturate the nitrogen gas with water vapor prior to streaming through cell 2 at a flow rate of 10-100 ml/min and stripping off the VOC from the water solution. Before entering the PTR-ToF-MS, the nitrogen gas flow, loaded with the stripped VOC, was diluted by adding 500-4500 ml/min nitrogen in order to reduce the humidity and adjust the VOC concentration to an optimal range for the measurement by PTR-ToF-MS. Both stripping cells were double jacketed glass cells being thermostated via a closed water circuit from an external thermostat (C25 / F6, HAAKE, Digitana AG). Cells were mounted insight an oven (UT 6420, Heraeus, Thermo Scientific, Switzerland) which was held at a temperature of +20°C above the temperature of the cells to prevent condensation in the tubing system. The whole setup is computer controlled. The automation allows controlling and adjusting all relevant parameters of the experiment (temperatures, flows), preparing the mixture of the aqueous VOC solution, filling as well as the cleaning stripping cells and conducting repetitions for a compound.

Figure 1: Experimental setup for measuring the air-water partitioning coefficients of volatile organic compounds. a) Schematic drawing of the automated measuring setup. b) PTR-ToF-MS. c) stripping cells insight the oven.

Results and Discussion

The temperature dependence of the Henry Law Constants of over 20 molecules was measured with a fully automated stripping cell setup with improved temperature and humidity controlled, extended temperature range and coupled to a PTR-ToF-MS. The HLC of a VOC can be derived from the PTR-ToF-MS measurements by monitoring the depletion of the signal intensity with time according to equation 1. A typical depletion signal is given in Figure 2. A VOC stripping experiments is automatically stopped once a depletion of 70% relative to the starting signal intensity is reached. The automated setup allows a sequential measurement of the HLCs at different temperatures and for different VOCs without human intervention.

$$\frac{dC}{dt} = \frac{-G \cdot C}{k_H \cdot V \cdot R \cdot T} \qquad \xrightarrow{\text{integration from } t=0 \text{ to } t=t} \qquad \ln\left(\frac{C}{C_0}\right) = \frac{-G}{k_H \cdot V \cdot R \cdot T} \cdot t \qquad \textit{Equation 1}$$

C: concentration of the VOC at time t; C_0: concentration of the VOC at time t = 0; G: gas flow through stripping cell; HLC: $k_H = c_a/p_g$ [mol/(m³·Pa)]; c_a: concentration of the analyte in the liquid phase; p_g: vapor pressure of the analyte in the gas phase; V: volume; R: ideal gas constant (8,314472 J·mol⁻¹·K⁻¹); T: temperature [K]; t: time.
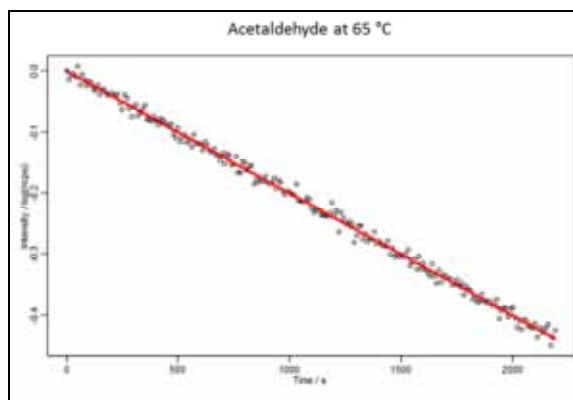
Figure 2: Depletion signal of acetaldehyde in water, measured with PTR-ToF-MS. This plot allows determining the HLC (k_H) from the slope.

The temperature dependence of the HLC is given by the van`t Hoff equation in equation 2.

$$\frac{d\ln k_H}{dT} = \frac{\Delta_{sol}H}{RT^2} \xrightarrow{\text{integration}} \ln k_H = \ln k_H^0 + \frac{\Delta_{sol}H}{RT^0} - \frac{\Delta_{sol}H}{R} \cdot \frac{1}{T} \qquad \textit{Equation 2}$$

$k_H = c_a/p_g$ [mol/(l·atm)]: HLC at temperature T; $k_H^0 = c_a/p_g$ [mol/(m³·Pa)]: HLC at temperature T^0; $\Delta_{sol}H$: solvation enthalpy; R: ideal gas constant (8,314472 J·mol⁻¹·K⁻¹); T: temperature [K]

In this study, the HLCs were measured in a temperature range of 4°C up to 85°C. A typical result of the temperature dependence of the HLC in this range is given in Figure 3 for the molecules 2,3-butanedione, acetaldehyde and methanethiol. The high accuracy of the measured data underlines the high precision of this improved setup for measuring the temperature dependence of the partitioning coefficients of VOCs in water. The automation of the setup allows a fast and continuous measurement of HLCs at various temperatures and can easily be applied to different solvents and matrices.
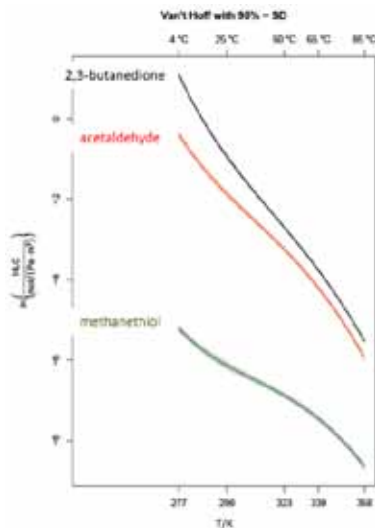
Figure 3: Temperature dependence of the HLC for 2,3-butanedione, acetaldehyde and methanethiol plotted according to the van`t Hoff equation. The shadowed curve corresponds to the 95% confidence interval.

References

[1] P. Pollien, C. Yeretzian; Liquid-Air Partition Coefficients of Coffee Flavour Compounds: A Novel Approach Using Proton-Transfer-Reaction Mass-Spectrometry. 19ème Colloque Scientifique International sur le Café; Trieste(Italy),14-18 Mai 2001; Association Scientifique International du Café (ASIC), Paris [http://www.asic-cafe.org], (2002).

[2] P. Pollien, A. Jordan, W. Lindinger, C. Yeretzian; Liquid-Air Partitioning of Volatile Compounds in Coffee: Dynamic Measurements using Proton-Transfer-Reaction Mass-Spectrometry; Int.J.Mass Spec. 228, 69-80, (2003).

[3] E. Schuhfried, F. Biasioli, E. Aprea, L. Cappellin, C. Soukoulis, A. Ferrigno, T. D. Maerk, F. Gasperi, PTR-MS measurements and analysis of models for the calculation of Henry's law constants of monosulfides and disulfides Chemosphere In Press, (2011).

[4] P. Pollien, C. Lindinger, A. N. Glöss, C. Yeretzian, Dynamic Approaches to Measure Partition Coefficients of VOCs: 4st International Proton Transfer Reaction Mass Spectrometry Conference; A. Hansel, T. Märk - Editors; Universitätszentrum Obergurgl, Obergurgl - Austria; 6th February - 21st February 2009; innsbruck university press, 2009, ISBN 978-3-902571-99-1, 221-226 (2009)pp. 221-225 (2009).

Emission of volatile organic compounds (VOC) by grapevine leaves in response to elicitor treatment and *Plasmopara viticola* inoculation

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Abstract

Downy mildew (*Plasmopara viticola*) is the most severe grape pathogen in North America and Europe. Infected plants reduce allocation of metabolites into the grapes resulting in lowered yield of grapes and due to delayed ripeness and lower sugar content also in reduced quality of the wine. This strong impact of downy mildew on grapes stimulates research on biological controls lowering fungal infection rates and/or stimulates plants' defence mechanisms. It has been shown that treatment of grapevine leaves with sulphated laminarin (PS3) can elicit resistance against *P. viticola* [1]. Transcriptomic data showed an up-regulated expression of grapevine terpene synthase and methylsalicylate transferase genes in response to elicitor treatment. To gain insight into the potential role of plant defensive volatile organic compounds (VOC) in grapevine defense against pathogens we used the PTRMS technique to monitor online the dynamics of VOC emission from grapevine leaves in response to treatment with PS3 and subsequent inoculation with *P. viticola*. Monitoring VOC emissions for four days after elicitor application and for three days after pathogen inoculation, respectively, we observed an induction of methyl salicylate (MeSA) and sesquiterpene emission initially by the elicitor treatment as well as by application of the surfactant (MOCK control) alone. The infestation of leaves with downy mildew spores one day later induced a second induction of MeSA at day 4 but did not affect mono- or sesquiterpenes emissions. Nevertheless, the elicitor treatment caused a reduction in pathogen infestation level.

These results combination with GC-MS data will elucidate if VOC could be suitable biomarkers of induced resistance in grapevine leaf / *Plasmopara viticola* (downy mildew) interaction.

References

[1] S. Trouvelot, A.-L. Varnier, M. Allègre, L. Mercier, F. Baillieul, C. Arnould, V. Gianinazzi-Pearson, O. Klarzynski, J.-M. Joubert, A. Pugin, and X. Daire, A β-1,3 glucan sulfate induces resistance in grapevine against *Plasmopara viticola* through priming of defense responses, including HR-like cell death. Molecular Plant-Microbe Interactions 21, 232-243, (2008).

Preliminary results of measurement of volatile compounds adsorbed on diesel exhaust particles by PTR-TOFMS

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Abstract

Diesel emissions consist of a large number of gaseous and particle-phase compounds. To investigate particle-phase organic compounds by PTR-TOFMS, sampled exhaust was passed through a heating tube to evaporate particle-phase compounds. By changing the heating temperature, concentration of particle-phase compounds are calculated from the difference of the 2 measurements. The results showed that particle-phase compounds include higher m/Z compounds in addition to gaseous compounds. PTR-TOFMS combined with a heating tube is expected to be useful to investigate emissions of particle-phase organic compounds.

Introduction

Emissions from modern diesel engines for automobiles were significantly reduced by progress in combustion technology and emission after treatment devices. Diesel emissions consist of a large number of gaseous and particle-phase compounds. PTR-TOFMS is a powerful tool to analyze gaseous organic compounds (i.e. volatile organic compounds). Particle-phase compounds also include organic compounds, so it is desirable to use PTR-TOFMS for analysis of particle-phase organic compounds. This paper shows preliminary results of analysis of particle-phase volatile compounds measured by PTR-TOFMS.

Experimental Methods

In this work, a HD diesel engine (displacement 3L with turbo-intercooler) was used to supply diesel exhaust to PTR-TOFMS. Experimental setup is shown Fig.1. Exhaust was sampled from an exhaust pipe to a partial flow dilution system. In the dilution system the sampled exhaust was mixed with dilution air and the dilution ratio DR was kept constant (15:1). The diluted exhaust was then split into 2 flows, one for PTR-TOFMS and the other for particle filter. The diluted exhaust for PTR-TOFMS was passed through a heating tube which enables particle-phase compounds to evaporate. Thus PTR-TOFMS is capable of analysis of particle-phase compounds in addition to gaseous compounds.

To investigate particle-phase compounds, 2 experiments were conducted. First, the heating tube was kept at lower temperature (ex. 100 degC) to analyze gaseous organic compounds. Second, the heating tube was kept at higher temperature (ex. 300 degC) to analyze gaseous and particle-phase organic compounds. The difference between 2 measurements was particle-phase compounds.
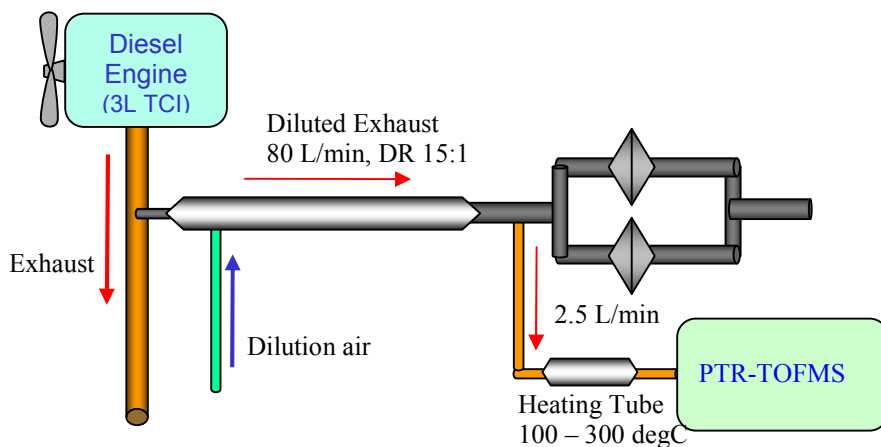
Figure 1: Experimental setup of diesel engine exhaust measurement by PTR-TOFMS.

Results and Discussion

The engine was operated at a ramped steady-state test cycle WHSC (World Harmonized Stationary Cycle) . Gaseous compound of VOCs (volatile organic compounds) showed stepwise change during the test cycle shown in Fig.2.
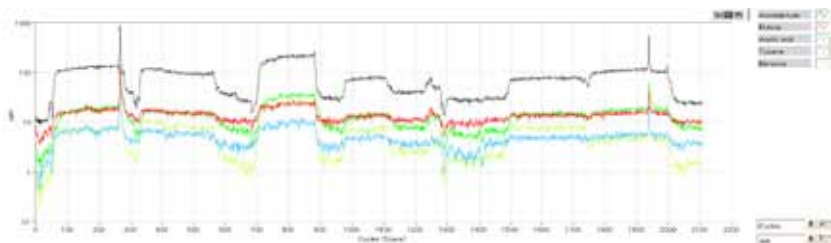
Figure 2: Concentration change of gaseous compounds of VOCs during WHSC.

Fig.3 shows the difference between TOF mass spectra heated at lower and higher temperature.

The TOF mass spectrum at higher temperature shows higher concentration and additional peaks at higher m/Z. These additional emissions are attributed from particle-phase compounds.
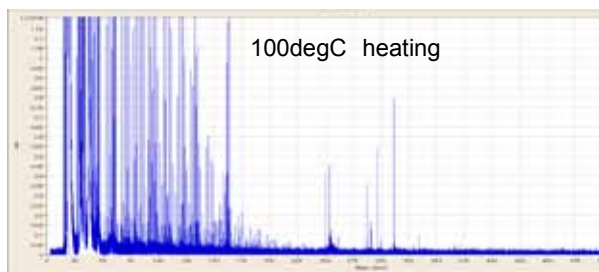
(a) TOF mass spectrum heating 100 degC
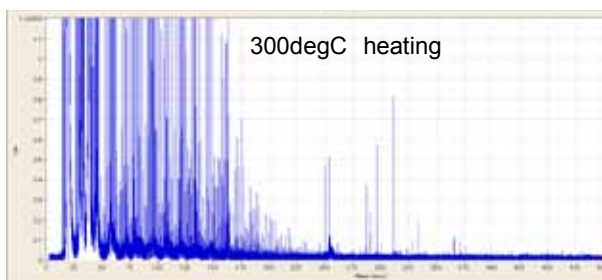
(b) TOF mass spectrum heating 300 degC

Figure 3: Averaged TOF mass spectra around 800 s of WHSC (a) gaseous compounds by heating 100 degC (b) gaseous and particle-phase compounds by heating 300 degC.

References

[1] Nobuhiro Yanagisawa, Keiko Shibata, Kenji Enya, and Kaoru Satou, Transient behavior of VOCs and particle emission from diesel engine equipped with diesel particulate filter, 5th International PTR-MS Conference (2011).

[2] Nobuhiro Yanagisawa, Keiko Shibata, Kenji Enya, Kaoru Satou, Transient Behavior of VOCs Emission and Particle Size Distribution during Active Regeneration of Diesel Particulate Filter Equipped Diesel Engine, SAE paper 2011-01-2087 (2011).

Index of Authors