First International Conference on Soft Chemical Ionisation Mass Spectrometry and Applications to Trace Gas Analysis

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Overview

The need for quantitative and rapid detection of chemical compounds in complex environments and at ultralow concentrations provides significant challenges to analytical chemistry for applications in many areas. Soft chemical ionisation mass spectrometric techniques can be used to address some of these challenges, and hence are key technologies for many analytical applications, ranging from atmospheric chemistry through to homeland security.

The aim of this conference is to provide a forum for discussions on research, instrumentation and applications of soft chemical ionisation mass spectrometric (SCIMS) techniques, with a particular focus on the technologies of PTR-MS, IMS, IMS/MS and SIFT-MS, covering many of areas of applications, but with an emphasis on **fundamental research and development, atmospheric chemistry, homeland security, and the environmental, food and health sciences.**

A key purpose of the conference is to bring together scientists and technologists from academia, industry and government who use SCIMS technologies in an informal setting to network and share details on recent advances and applications. An objective of this meeting is to facilitate closer collaboration and to improve the exploitation of novel concepts between disciplines and technologies.

Young scientists (e.g. Early Stage Researchers and PhD students) at the beginning of their research careers are particularly encouraged to attend and contribute to the meeting, either with a poster or with an oral presentation.

Dornbirn

Dornbirn is situated in the beautiful Vorarlberg region of Western Austria near Lake Constance, just a few kilometres from the Swiss border, offering scenic tours of the Alps. There are excellent and fast train connections from many nearby major cities, including Zurich, Munich and Innsbruck.

Programme

The conference will begin Monday morning (8:45 am) and finish Wednesday late afternoon (5 pm). The program includes invited talks by distinguished leaders using SCIMS covering various research fields; including environmental science, atmospheric chemistry, food science, health science and homeland security. The conference will also include invited short talks and a poster session. (Please state in any abstract submission if you wish to be considered for a talk, a poster or both.) For young researchers, there will be an interactive session on careers within academia, industry and the government.

Abstracts

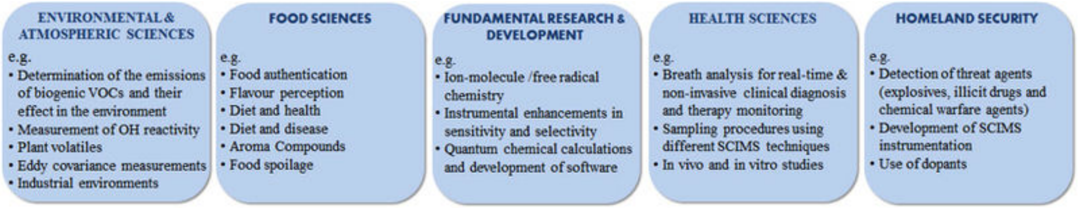
Abstract submissions should be sent to Professor Karl Unterkofler, karl.unterkofler@fhv.at (mailto:karl.unterkofler@fhv.at)(deadline 15th August 2017). Abstracts should be no more than one side of A4 using font size 12 including graphs and figures. Most abstracts will be accepted for posters, a number will be selected for oral presentation.

Registration

The registration fee is only €60 to include a conference dinner and coffee breaks.
To register please go to veranstaltungen.fhv.at/CSCIMS (http://veranstaltungen.fhv.at/CSCIMS/) by the 31st August 2017. We are grateful for support from HORIZON 2020 EU ITN “IMPACT” (Ion Molecule Processes for Analytical Chemical Technologies Network, GA 674911), the University of Innsbruck, the Molecular Physics Group of the Institute of Physics (UK), and the FHV, which has enabled us to keep the registration fee low.

Accommodation

As a guest of the Fachhochschule Vorarlberg you will be able to get specials rates at Hotel Krone en.kronehotel.at. (http://en.kronehotel.at/.) When booking with the Hotel Krone, please state “Gast der Fachhochschule Vorarlberg”. There are also many other hotels in Dornbirn and the surrounding area. Please e-mail Prof. Unterkofler if you need any assistance. It is advisable to book an hotel from Sunday the17th September.



ENVIRONMENTAL & ATMOSPHERIC SCIENCES

e.g.
- Determination of the emissions of biogenic VOCs and their effect in the environment
- Measurement of OH reactivity
- Plant volatiles
- Eddy covariance measurements
- Industrial environments

FOOD SCIENCES

e.g.
- Food authentication
- Flavour perception
- Diet and health
- Diet and disease
- Aroma Compounds
- Food spoilage

FUNDAMENTAL RESEARCH & DEVELOPMENT

e.g.
- Ion-molecule /free radical chemistry
- Instrumental enhancements in sensitivity and selectivity
- Quantum chemical calculations and development of software

HEALTH SCIENCES

e.g.
- Breath analysis for real-time & non-invasive clinical diagnosis and therapy monitoring
- Sampling procedures using different SCIMS techniques
- In vivo and in vitro studies

HOMELAND SECURITY

e.g.
- Detection of threat agents (explosives, illicit drugs and chemical warfare agents)
- Development of SCIMS instrumentation
- Use of dopants

Confirmed Invited International Speakers

- **Franco Biasioli** (Fondazione Edmund Mach-Istituto Agrario di S. Michele, Italy)
  Food volatilomics by direct injection mass spectrometry
- **Simona M. Cristescu** (Radboud University, Holland)
  Sniffing the chemical language of plants and microorganisms
- **John M. Dyke** (Southampton University)
  Calculation of rate coefficients of radical -molecule reactions of importance in atmospheric chemistry and their measurement with photoionization
- **Julian King** (ZFF)
  Mathematical Modelling for Breath Gas Analysis
- **Pawel Mochalski** (Institut Breath Research, University of Innsbruck, AT)
  Monitoring of selected volatile organic compounds released by hidden humans using gas chromatography ion mobility spectrometry
- **Jochen Schubert** (Universitätmedizin Rostock, Germany)
  Applications of Soft Chemical Ionisation Mass Spectrometry for Clinical Breath Analysis
- **Patrick Sears & Peter Hickey** (Dstl, UK)
  Ambient ionisation techniques and homeland security, & spectrometry for security applications
- **Patrik Spanel** (Academy of Sciences of the Czech Republic Research Institute)
  Selected Ion Flow Tube Mass Spectrometry, SIFT-MS: from plasma physics via analytical chemistry to medicine
- **Jonathan Williams** (Max Planck Gesellschaft zur Förderung der Wissenschaften E.V.)
  Proton Transfer Reaction Mass Spectrometry and Atmospheric Chemistry

http://impact-h2020itn.com/events-page/ (http://impact-h2020itn.com/events-page/)

Detailed Programme

Monday 18th September	
8:15 – 8:45	**Registration**
8:50 – 9:40	**Introduction & Opening Address (Organisers)** ***Applications: Health and Life Sciences*** ***Chair: Karl Unterkofler*** **Jochen Schubert** (University Medical Centre Rostock, Germany) *Applications of Soft Chemical Ionisation Mass Spectrometry for Clinical Breath Analysis*
9:40 – 10:10	**Jan Rozman** (Helmholtz Institute, München, Germany) *A systemic view on exhaled volatile organic compounds in mice: a promising new level in the world of pan-omics*
10:10 - 10:40	**Pawel Mochalski** (Institut for Breath Research, University of Innsbruck, Austria) *Monitoring of selected volatile organic compounds released by hidden humans using gas chromatography ion mobility spectrometry (GC-IMS)*
10:40 - 11:00	**Giovanni Pugliese** (University Medical Centre Rostock, Germany) *Real time calibration of aliphatic amines*
11:00 - 11:30	Coffee Break
11:30 - 11:50	**Official Welcome** Rektor Tilmann Märk, Universität Innsbruck Landesrätin Dr. Bernadette Mennel FH-Rektorin Dr. Tanja Eiselen
11:50 – 12:30	**Simona M. Cristescu** (Radboud University, Netherlands) *Sniffing the chemical language of plants and microorganisms*
12:30 – 13:30	Lunch
13:30 - 14:00	**Julian King** (ZF Friedrichshafen, D) *Mathematical Modelling for Breath Gas Analysis*
14:00 - 14:30	**Kseniya Dryahina** (J. Heyrovsky Institute of Physical Chemistry of the CAS, Czech Republic) *Inflammatory bowel disease: SIFT-MS quantification of volatile metabolites in breath*

Tuesday 19th September	
8:30 – 9:15	**An interactive Session for Young Scientists: Careers – academic, industrial and governmental perspectives** Commercial Companies: IONICON (Rene Gutmann), KORE (Fraser Reich), MassSpecpecD BV (Maurice Janssen); Governmental: DSTL (Pete Hickey & Peter Sears); Academia (John Dyke, Paul Scheier)
9:15 - 9:45	**Fundamental Science** **Chair John Dyke** **Maurice H M Janssen** (MassSpecpecD BV, Nijmegen, Netherlands) *Direct enantiomer selective Mass Spectrometry of chiral mixtures by MS-PECD*
9:45 - 10:15	**Tom Field** (Queen’s University, Belfast, UK) *How Soft is Electron Attachment?*
10:15 - 10:45	**Instrumental Developments** **Chair Fraser Reich** **Rene Gutmann** (IONICON Analytik GmbH, Austria) *PTR-TOF-MS: Latest Improvements in Selectivity and Sensitivity*
10:45 - 11:15	**Robert Blake** (University of Leicester, UK) *CF3+ and CF2H+ as reagents for chemical ionization reaction mass spectrometry*
11:15 - 11:45	Coffee Break
11:45 - 12:15	**Štefan Matejčík** (Comenius University in Bratislava) *IMS and IMS-oaTOFMS detection of VOCs*
12:15 - 12:35	**Michal Lacko** (J. Heyrovsky Institute of Physical Chemistry of the CAS, Czech Republic) *Presence of water clusters in SCIMS*
12:40 – 13:30	Lunch
13:30 - 13:50	**Food Science** **Chair: Simona Cristescu** **Iuliia Khomenko** (Fondazione Edmund Mach (FEM), Italy) *High-throughput on-line monitoring of microorganism of*

Wednesday 20th September	
9:00 - 9:50	**Food Science** **Chair: Simona Cristescu** **Franco Biasioli** (Fondazione Edmund Mach (FEM), Italy) *Food volatilomics by direct injection mass spectrometry*
9:50 – 10:10	**Michele Pedrotti** (FEM, Italy) *The good, the bad and the aged: quality control of anhydrous milk fat through Proton Transfer Reaction Mass Spectrometry*
10:10 - 10:35	**Environmental Science & Atmospheric Chemistry** **Chair Jonathan Williams** **Dusan Materic** (Utrecht University, Netherlands) *Characterisation of the semi-volatile component of Dissolved Organic Matter by Thermal Desorption – PTR-ToF-MS*
10:35 - 11:00	**Luca Cappellin** (FEM, Italy & Harvard, USA) *Modern ultra-high sensitive SCIMS allows unprecedented studies in atmospherebiosphere interactions*
11:00 - 11:30	Coffee Break
11:30 - 11:50	**Charel Wohl** (Plymouth Marine Laboratory, UK) *Are the polar seas a net source or sink of Oxygenated Volatile Organic compounds (OVOCs)?*
11:50 – 12:10	**Illia Zymak** (J. Heyrovsky Institute of Physical Chemistry of the CAS, Czech Republic) *Study of gas-phase ion molecular reactions relevant to the atmosphere of Mars*
12:10 - 12:55	**Health Science** **Patrik Spanel** (J. Heyrovsky Institute of Physical Chemistry of the CAS, Czech Republic) *Selected Ion Flow Tube Mass Spectrometry, SIFTMS: from plasma physics via analytical chemistry to medicine*
13:00 – 14:00	Lunch
14:00 - 14:20	**Environmental Science & Atmospheric Chemistry** **Chair Chris Mayhew**

14:30 – 15:15	**Homeland Security** **Patrick Sears and Peter Hickey** (Dstl, UK) *Ambient ionisation techniques and homeland security*
15:15 - 15:45	Coffee Break
15:45 - 16:30	**Fundamental Science** **Chair John Dyke** **Paul Scheier** (Institut für Ionenphysik und Angewandte Physik, University of Innsbruck, Austria) *Electron driven reactions in doped He nanodroplets*
16:30 - 18:15	Poster Session
19:30–21:30	Conference Dinner

	relevance in food technology by PTR-ToF-MS
13:50 - 14:10	**Shazia Zafar** (University of Birmingham, UK) *A PTR-MS Study of Manuka Honeys*
14:30 - 15:15	**Environmental Science & Atmospheric Chemistry** **Chair Jonathan Williams** **John Dyke** (University of Southampton, UK) *Calculation of rate coefficients of radical-molecule reactions of importance in atmospheric chemistry and their measurement with photoionization*
	Free time to visit to Dornbirn, Bregenz, Lake Constance

	Felix Piel (IONICON Analytik GmbH, Austria) *Analysis of gasoline & diesel exhaust using SRI-PTR-TOFMS*
14:20 - 14:40	**Daniel Blenkhorn** (University of Birmingham, UK) *Detection and Sensitivity of Poly Aromatic Hydrocarbons measured by PTR-MS*
14:40 - 15:30	**Jonathan Williams** (Max Planck Institute for Chemistry, Air Chemistry, Germany) *Exploring air chemistry with a PTR-MS*
15:30 - 15:40	**Closing Remarks**

Organisation

The conference is co-organized and co-hosted by the Institute for Breath Research, University of Innsbruck, and the FH Vorarlberg, University of Applied Sciences.

Local Organisers:

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First International Conference on Soft Chemical Ionisation Mass Spectrometry and Applications to Trace Gas Analysis

18.-20. September 2017

Contents

Food volatilomics by direct injection mass spectrometry

Franco Biasioli

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Abstract

Volatile compounds play a relevant role in most steps of the food production chain: for instance, they are important metabolites of crop physiology, they drive and are released by fruit ripening and storage and they control the way we perceive food. Moreover, being spontaneously and continuously released, volatile compounds provide a non-invasive and rapid tool for the control of food samples and the real-time monitoring of biological and technological processes. The analysis of food volatile compounds is thus of outmost importance, mostly in an omic context. However the necessity of high throughput and of monitoring fast processes and very low concentrations poses some strict requirements: i) high sensitivity, ii) large dynamic range, iii) fast and iv) non-invasive measurements. These issues can be efficiently addressed by different Direct Injection Mass Spectrometry (DIMS) methods developed for volatile compound analysis, Proton Transfer Reaction Mass Spectrometry (PTR-MS) in particular. The lack of specificity of these techniques, as compared with chromatographic ones, is compensated by other features: they are very fast, non-invasive and provide high sensitivity even without sample pretreatment. This contribution aims at pointing out DIMS pros and cons in food volatilomics by describing few selected applications investigated at the Volatile Compound Facility at FEM and, in particular, that they can be used not only for real time monitoring but also for the accurate and highly informative characterization of samples. Three different applications are discussed: the screening of large datasets also in relation with genomic or sensory characterization, the on-line monitoring of processes of relevance for food technology, namely fermentation and backing, the investigation of food-consumer interaction by measuring nose-space concentration of volatile compounds Some recent developments which should increase specificity and sensitivity of PTR-MS based methods without compromising its positive features are also described.

CF3+ and CF2H+ as reagents for chemical ionization reaction mass spectrometry.

Robert Blake, University of Leicester, UK

Chemical Ionization (CI) is a blanket description for a collection of chemical processes, which produce low energy ionization reagents. In many CI schemes detection of the C_2-C_6 alkanes is difficult or impossible due to fragmentation or minimal sensitivity. Of the most commonly used CI reagents used in the PTR/SRI-MS/CIR-MS environment, H_3O^+ or NO^+ show little or no reaction, while O_2^+ reacts with all short-chain ($<C_6$) n-alkanes but causes severe fragmentation. A suitable CI scheme should be able to produce measurably less fragmentation than O_2^+ and react with all C_2-C_6 alkanes with similar sensitivity in a Chemical Ionization Mass Spectrometric (CI-TOF-MS) environment with factors such as high moisture content, operating pressures of 1–10 Torr, accelerating electric fields (E/N) and long-lived intermediate complex formation. The ion products produced from using CF_4 as a precursor, namely CF_3^+ and CF_2H^+ meet these requirements. The three most prominent CI processes are proton transfer, charge transfer and hydride extraction with the latter being the preferred route for the reaction of CF_3^+ with the lighter n-alkanes. Another characteristic of CF_3^+ is its strong electrophilic behavior with aromatics and nitriles, where the electron withdrawing power of the three fluorine atoms in CF_3^+ exceeds its electron donating power, so that it acts as a strong Lewis acid.

A comparison of the reactions of CF_3^+ and O_2^+ with dry gas mixtures of ethane, propane, butane, pentane and hexane at E/N of 50 and 100 Td showed that O_2^+ caused significantly more fragmentation than CF_3^+ in all cases. When CF_3^+ reacts with traces of H_2O to form CF_2H^+ and H_3O^+, the outcome is influenced by relative humidity and E/N. When RH is 0% and E/N > 120 TD the ratio of CF_2H^+ / CF_3^+ is less than 1%. On the other hand, for high RH and E/N < 80 Td the CF_3^+ yield is severely depleted and drops below 5% of its initial value in dry conditions.

In experiments on a selection of common VOCs, simultaneous measurements were made on two identical TOF-MS, one using H_3O^+ for a traditional PTR view and the other using CF_3^+. The twin outcomes provided relative yields and fragmentation behaviour in the two environments as well as giving an estimate of the actual PTR contributions present in the CF_3^+ spectra. Examples of oxygen substitution were observed in short chain aldehydes and ketones. Lewis acid behaviour of CF_3^+ occurred with some common aromatics and nitriles. VOCs with longer alkyl groups tended to favour chain fragmentation over other alternative reaction modes.

There are two areas where CF_3^+ and CF_2H^+ are proving to be useful tools. The first of these is in breath analysis of cigarette smokers where ethane and pentane are believed to be important constituents. Another application they are proving useful in is estimating total organic carbon content in oil shale. Owing to the fragmentation inherent in the larger alkanes, it was sufficient to consider the yields up to C_4 to account for over 90% of the yield. In both these instances, the ambient humidity is high and it was found to be necessary to take account of contributions from H_3O^+ as well as the main CI reagent. As H_3O^+ was found to be produced by a two-stage reaction, its contribution to the observed spectra was not large, but significant nonetheless. The analysis of complex mixtures in smoker's breath is the subject of an investigation for a PhD thesis and an early example of the results are shown.

Detection and Sensitivity of Poly Aromatic Hydrocarbons measured by Proton Transfer Reaction – Mass Spectrometry

Daniel Blenkhorn[1,2], Fraser Reich[3], Rob Mackenzie[1], William Bloss[1] and Chris A. Mayhew[2]

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Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is an analytical technique used for the detection, monitoring and quantification of volatile organic compounds (VOCs). Owing to the benefits of soft chemical ionisation, PTR-MS has found applications in many fields, such as environmental analysis, health and food sciences and homeland security. Within the environmental sciences, PTR-MS is commonly employed in the real-time quantification of biogenic emissions such as isoprene and monoterpenes for ecosystem flux measurements, but has also found to be effective for measurement of anthropogenic emissions such as benzene and toluene.

In the environmental sciences, the reactions of reagent ions with VOCs have been studied extensively [1]. However, for those compounds with lower vapour pressures such as semi-volatile organic compounds (SVOCs), there has been less studies on their detection and quantification. Recent improvements to PTR-MS instrumentation have allowed SVOCs to be detected by interfacing rapidly heated desorbers with heated inlet lines to modified drift tubes which can be heated to 200°C.

In this study, we report the use of a Radio Frequency Ion Funnel (RFIF) PTR-MS drift tube to increase the sensitivity for the detection of Poly Aromatic Hydrocarbons (PAHs). We focus particularly on benzo[a]pyrene ($C_{20}H_{12}$, m/z 253.09) which is used as a representative PAH by the European Union, as stated in directive 2004/107/EC [2]. Following proton transfer from H_3O^+ the dominant product ion observed is the protonated molecular ion $(C_{20}H_{12})H^+$. We present details on the ionisation mechanisms, detection and sensitivity of PAH standards, with a forward look to developing the detection method into one suitable for on line whole air sampling.

[1] Ellis, A. and C. Mayhew, Proton Transfer Reaction Mass Spectrometry - Principles and applications. 1st ed. 2014: Wiley.
[2] EU Directive 2004/107/EC http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32004L0107

First International Conference on Soft Chemical Ionisation Mass Spectrometry and Applications to Trace Gas Analysis

Variability of OH reactivity in a Pine forest: Preliminary results from the LANDEX experiment in July 2017

Sandy BSAIBES, V. Gros, F. Truong, S. Dusanter, S. Sauvage, K. Mermet, T. Leonardis, N. Locoge, J. Kammer, P.M. Flaud, E. Perraudin and E. Villenave

On the global scale, biogenic volatile organic compounds (BVOCs) emitted mainly by the vegetation, exceed by a factor of 10 those from anthropogenic sources. BVOCs include isoprene, monoterpenes, sesquiterpenes, and a number of oxygenated compounds presenting relatively high atmospheric reactivity. Thus, they may play an important role in the tropospheric chemistry, and in forested areas they contribute largely to the OH reactivity (which represents the main OH sink).

As part of the LANDEX field campaign, our study took place in a Pine forest located in The Landes area, in Southwestern France during the June-July 2017 summer period.

Atmospheric mixing ratios of biogenic compounds were measured using gas chromatographs (GC-FID and GC-MS) as well as a time of flight- proton transfer reaction mass spectrometer (PTR-TOFMS) and total OH reactivity was measured based on the comparative reactivity method (CRM).

Air masses were sampled at two heights: 4 m and 12 m, respectively inside the cover and above the canopy. OH reactivity diurnal cycle and vertical gradient will be presented in relation with the BVOCs variability. Preliminary results show that the OH reactivity measured at the site mainly depended on the main primary biogenic species emitted by the forest (i.e. α and β-pinene).

Keywords: OH reactivity, BVOCs, CRM, PTR-TOFMS, Pine forest

Modern ultra-high sensitive SCIMS allows unprecedented studies in atmosphere-biosphere interactions

L. Cappellin[1,2], V. Giacomuzzi[3], S. Angeli[3], F. Biasioli[2], and K. McKinney[1]

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Abstract

In nature, volatile organic compounds (VOCs) play a crucial role in mediating many interactions between the biosphere and the atmosphere. Modern instruments based on soft chemical ionization mass spectrometry (SICIMS) allow investigation of such processes providing remarkable insights.

In this contribution, we present a series of field and laboratory studies, highlighting the unique performance provided by SICIMS.

In a first work, we show that bidirectional fluxes of benzenoid compounds could be detected for the first time in a New England forest [1]. In a second study, we demonstrate that important crops in Europe, including grapevine and apple, are able to sequestrate harmful VOCs from the atmosphere, detoxify them, and emit less harmful compounds. In another series of experiments we investigated the response of grapevines and apple plants grown under control conditions to several herbivore insect attacks. Different herbivore-induced volatiles were characterized depending on the fruit crop and on the specific interaction with the pest insect. These included green leaf volatiles, terpenoids, benzenoid, and sulphur compounds [2]. Several compounds of interest in these studies required detection capabilities in real-time and in the pptv range.

References

[1] L. Cappellin, A. Algarra Alarcon, I. Herdlinger-Blatt, J. Sanchez, F. Biasioli, S.T. Martin, F. Loreto, K.A. McKinney, Field observations of volatile organic compound (VOC) exchange in red oaks, Atmos. Chem. Phys. 17 (2017) 4189–4207. doi:10.5194/acp-17-4189-2017.

[2] V. Giacomuzzi, L. Cappellin, I. Khomenko, F. Biasioli, S. Schütz, M. Tasin, A.L. Knight, S. Angeli, Emission of Volatile Compounds from Apple Plants Infested with Pandemis heparana Larvae, Antennal Response of Conspecific Adults, and Preliminary Field Trial, Journal of Chemical Ecology. 42 (2016) 1265–1280. doi:10.1007/s10886-016-0794-8.

BIOGENIC VOLATILE ORGANIC COMPOUNDS EMISSIONS AND OZONE UPTAKE ON SOIL SURFACES

Raluca Ciuraru, Florence Lafouge, Céline Decq, Olivier Fanucci, Olivier Zurfluh, Jean-Christophe Gueudet, Sophie Genermont, Benjamin Loubet

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Agricultural lands occupy about 40-50% of the Earth's land surface. In order to assess the potential of agricultural ecosystems acting as a source or sink for ozone and biogenic volatile organic compounds (BVOC), it is necessary to determine the emissions and deposition at soil-atmosphere interface.

Although the role of the vegetation in these processes has been extensively studied, the role of soil and soil organic matter content has been less studied. BVOCs play a key role in tropospheric chemistry contributing to the formation of secondary pollutants like ozone. Ozone is of major importance in tropospheric chemistry, at high concentrations near the surface being harmful to humans and vegetation. Understanding the interactions of ozone at soil surfaces will then improve our knowledge of the ozone budget. Generally, the ozone deposition is quantified via above-canopy measurements but such observations provide little information concerning the underlying sources and sinks. Stomatal fluxes generally account for 30–70% of the observed above-canopy ozone flux while the "non-stomatal" ozone budget has been assigned to physical and chemical processes, i.e. surface reactions or gas-phase reactions with BVOCs[1].

This study investigates the ozone uptake and deposition on soil surfaces using a soil chambers method and a high sensitivity proton transfer reaction mass spectrometer. Preliminary results showed that the reactions of ozone at this interface occur via two simultaneous mechanisms: a heterogeneous reaction strictly on the surface and a homogeneous reaction occurring in the gas phase. The relative rates of these two processes will be presented and discussed.

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[1] G. M. Wolfe et al, Atmos. Chem. Phys., 11, 7875–7891, 2011

Sniffing the chemical language of plants and microorganisms

Simona M. Cristescu

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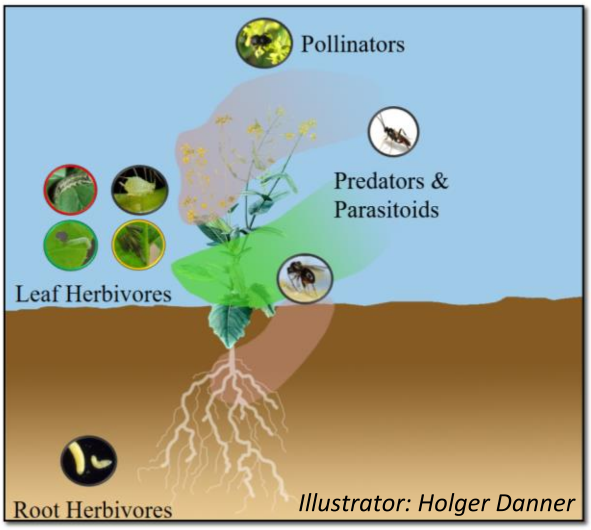
All organisms including, humans, animals, plants, fungi and bacteria, commonly produce volatile organic compounds (VOCs). They diffuse easily into the surrounding environment, via air- and gas- filed pores and play important role in the communication and interaction between species.

Scents from flowers serve to attract pollinators. However, also leaves or roots of plant emit VOCs that increase in emission rates and diversify upon (root) herbivore attack[1]. It is amazing how plants respond to their environment, although they don't have eyes, mouths or nervous system. Yet they are capable of determining who is attacking them. An infochemical web between plants, herbivores and herbivore enemies is created[2,3].

In this talk, I aim to provide succinct summary of the most common volatiles produced by plants and microorganism (such as sulfur VOCs, terpenes, nitrogen VOCs), their ecological role and importance in above- and belowground interspecies interactions and communication[4]. Furthermore, I will review current most promising approaches for sampling and measuring volatile and will highlight the potential of volatiles as biomarkers.



Illustrator: Holger Danner

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[1] Danner *et.al.*, J. Chem. Ecol. 41: 631-640 (2015)

[2] Desurmont *et.al.*, Plant, Cell & Environment 37, 1854–1865 (2014).

[3] Danner *et.al.,* New Phytologist doi:10.1111/nph.14428 (2017)

[4] Van Dam *et. al.*, Deciphering Chemical Language of Plant Communication, Signaling and Communication in Plants, doi 10.1007/978-3-319-33498-1_8 (2016)

Limitations of E/n plots in Soft Chemical Ionisation Mass Spectrometry (SCIMS)

Renaud Dassonville, Kore Technology, UK

Soft Chemical Ionisation Mass Spectrometers (SCIMS) are becoming ever more useful in molecular identification in different fields of research such as the Environment, Medicine and Homeland Security. These instruments offer many advantages over quadrupole-based instruments, and more recently a new technology, the RF ion-funnel, has been installed on these instruments, increasing their sensitivity.

In order to understand better the effects of employing RF fields on the product ions in SCIMS, we have conducted a detailed study of two analyte molecules in the standard case in which there is only a linear electric field in the chemical ionisation reactor. By characterising the behaviour of these molecules under many different conditions in the linear electric field, our aim was to map out the parameter space so that we could then compare data produced when using the RF funnel (and thus deduce the effect of the RF fields). However, even with the simple case of a linear electric field, the data we have obtained is not sufficiently explained by plotting the ratios as a function of the Townsend number, E/n. Data acquired with the same calculated E/n, but using different pairs of temperature and pressure, do not overlay. The ratios of the product ions (the "branching ratios") vary according to how the E/n is achieved. In this presentation we will demonstrate this effect by presenting detailed branching ratio data for n-Butylbenzene (nBB) and Triethyl Phosphate (TEP) over a wide range of E/n values, and with variations in the reactor of temperature and pressure.

In practice, if data is produced from a SCIMS instrument with invariant conditions then the data will be comparable. However, when comparing data from different instruments, or indeed from the same instrument with nominally the same E/n but with different reactor conditions, then the data is not strictly comparable. Researchers should be aware of these limitations. What has become clear is that we need a more precise way to describe the effective temperature of the collisions inside the reactor. We are now considering a new theoretical approach to this issue and hope to report on this at a later date.

Inflammatory bowel disease: SIFT-MS quantification of volatile metabolites in breath.

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Inflammatory bowel diseases (IBD) affect the colon and small intestine and include Crohn's disease (CD) and ulcerative colitis (UC). IBD falls into the class of autoimmune diseases in which the body’s own immune system attacks parts of the digestive system and it is associated with environmental and genetic factors. There is no cure for IBD, but current medical therapy can alleviate the symptoms. The frequently used therapeutic monitoring methods are invasive including endoscopy or imaging procedures and thus there is a growing interest in non-invasive breath analysis approach [1, 2]. For example n-pentane in breath is considered to be a produced by lipid peroxidation and can be elevated in inflammatory conditions such as IBD (see Figure 1). Selected ion flow tube mass spectrometry SIFT-MS is suitable for quantification of multiple volatile metabolites in breath. The IBD study including 136 CD and 51 UC patients serves as an illustrative example of relating metabolite concentrations to the underlying metabolic changes. In addition to pentane elevated concentrations were observed of hydrogen sulphide, acetic acid, propanoic acid and butanoic acid in the exhaled breath of the CD and UC patients.

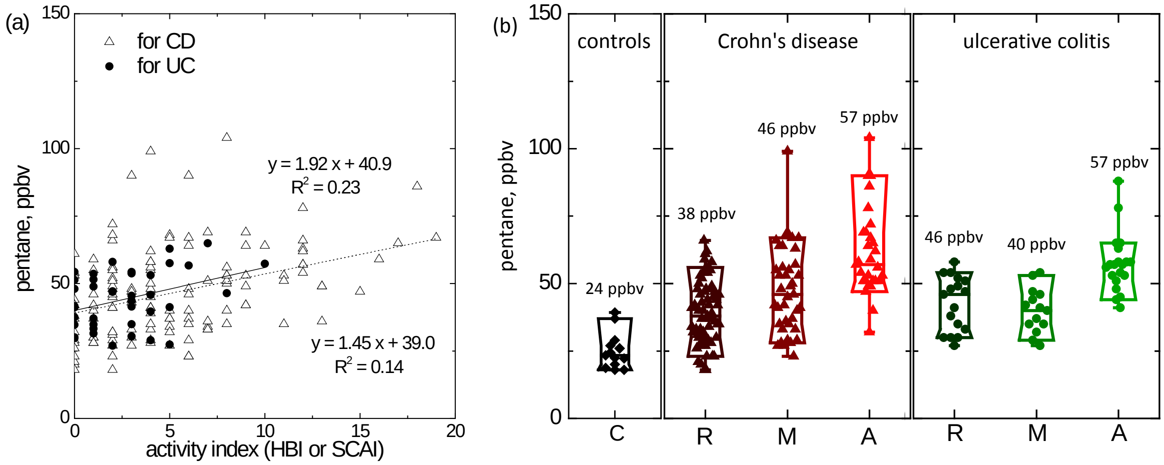

Figure 1. (a) Correlation of exhaled pentane with the appropriate activity index. (b) Box-and-whisker plots of breath pentane concentrations for controls (C) and the remission (R), mild to moderate active disease (M) and severe active disease (A) groups of Crohn’s disease and ulcerative colitis patients.

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Calculation of rate coefficients of radical-molecule reactions of importance in atmospheric chemistry and their measurement with photoionization

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This presentation will outline how mechanisms and channel specific rate coefficients of atmospherically relevant radical-molecule reactions can be determined by combining experimentally measured values, from photoelectron experiments, and calculated values from surfaces derived from electronic structure calculations. The channel specific rate coefficients will be needed for local, regional and global scale atmospheric models.

The theoretical part of the project involves two parts (i) calculation of a potential surface for the reaction and (ii) calculation of rate coefficients, at the high pressure limit, using that surface. For (i), for medium-sized reaction systems (10-30 atoms), practical computational strategies at current state-of-the-art levels are based on those of composite methods, which employ lower levels for geometries and vibrational frequencies, and a higher level for relative energies. For (ii), variational transition-state-theory (VTST) is used with incorporation of tunnelling corrections. After reviewing briefly the main electronic structure methods used, the main features and assumptions of TST will be outlined and ways of improving TST, by using VTST, will be summarised. These calculations support the experimental part of the project by providing, for each reaction, reliable channel specific rate coefficients and branching ratios, and an understanding of the reaction mechanism.

A summary will be given of the apparatus used to measure rate coefficients. It consists of a flow-tube interfaced, via a differential pumping system, to a photoelectron spectrometer designed to study short-lived reactive intermediates in the gas-phase. Experiments are carried out under laminar flow conditions and the kinetics measurements are made under pseudo first-order conditions with one reactant in excess. The main features of this combined theoretical and experimental research will be highlighted by considering a number of examples.

How Soft Is Electron Attachment?

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Free electrons with 0-10 eV can attach to molecules and form negatively charged ions by, for example, dissociative electron attachment. At low energies below 1eV the process may be soft and not lead to any molecular fragmentation and have very large cross sections. Low energy electrons may also cause energetic molecular fragmentation.

The softest electron attachment processes leading to negative ion formation are when the electron is transfered from a negative ion or Rydberg state to form a dipole bound negative ion state. The formation of dipole bound states in negative ion collisions will be considered; H^- and O^- impact on acetonitrile has led to formation of negatively charged dipole bound states of acetonitrile.

The practicalities of using electron attachment as a bulk/macroscopic process for formation of negative ions will be considered. The ease of generation of electron beams make them a potentially attractive ionization source, but their application for soft ionization may be restricted to certain families of molecules.

Ion Funnel meets Ion Guide: Improving the Sensitivity and Selectivity of PTR-TOFMS for real-time analysis of VOCs

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The transfer region between the chemical ionization chamber (drift tube) and the Time-of-Flight (TOF) mass analyzer is one of the most crucial parts affecting the sensitivity of a Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) instrument. Ion funnels which are focusing devices consisting of a series of lenses with successively smaller apertures and applied RF voltages are one powerful way to improve the ion transmission by orders of magnitude.
Here we present a modular ion funnel design, which can be installed adjacent to the drift tube of a conventional PTR-MS instrument. Installing the modular ion funnel increases the sensitivity by a factor of about 5-10. In case of the novel high-end instrument PTR-TOF 6000 X2 the ion funnel is complemented by a hexapole ion guide. This combination increases the sensitivity even further and additionally improves the mass resolution to up to 6000 $\Delta m/m$.
With the ion funnel turned on, the instrument is extremely sensitive and can quantify compounds down to very low concentrations. Switching the RF supply of the ion funnel off artificially lowers the sensitivity, so that saturation effects can be avoided for high concentrations (Figure 1).
We conclude with a study, which indicates that neither the ion funnel nor the hexapole ion guide make the ion chemistry in the drift tube over-complicated. Thus the E/N is well-known and E/N studies can easily be performed.

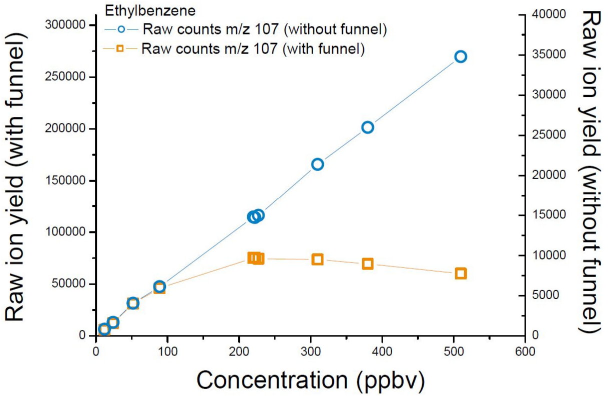

Figure 1: Extension of the dynamic range by switching the funnel on and off.

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Ben Henderson

An Investigation into the origin of VOCs

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Exhaled breath contains thousands of useful bits of information, namely volatile organic compounds (VOCs). One of the major benefits of this is the potential to use these VOCs as biomarkers for disease treatment and monitoring. There have been many pilot studies in identifying VOCs as biomarkers for diseases. However we are not at the point of wide clinical use, this is for a number of reasons. Perhaps most importantly a lack of standardisation within the breath analysis community on sampling methods and analysis. One of the goals of this PhD is to work in collaboration within the International Association of Breath Research (IABR) on a benchmarking study that will help take the first steps on the road towards standardising breath sampling. In addition to identifying the VOCs it is important to know where they are coming from, as a result the origin of VOCs in children with asthma will be investigated in collaboration with the AMC on the Microbiome Asthma Prevention Study (MAPS). This will be achieved by combining in vivo (exhaled breath samples, air from lungs during bronchoscopy) and in vitro (cell cultures, microbiome) analysis to discover the origin of the VOCs.

Direct enantiomer selective Mass Spectrometry of chiral mixtures by MS-PECD

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Mass Spectrometry is chirally blind, it cannot directly distinguish the two enantiomers of chiral molecules. Simultaneous, enantiomer-specific identification of chiral molecules in multi-component mixtures is extremely challenging. Here we show how enantiomers may be differentiated by Mass-Selective PhotoElectron Circular Dichroism (MS-PECD) using an electron–ion coincidence imaging spectrometer [1-3]. Following an ionizing circular polarized laser pulse, ions and electrons are detected in coincidence on their respective time- and position sensitive detectors. The Mass-Selected PECD asymmetry reveals that the compound is chiral. Here we will present the latest results with regard to the fundamental developments in PECD and the extension to analytical applications employing direct Mass Spectrometry analysis of multi-component mixtures of chiral molecules [4-6].

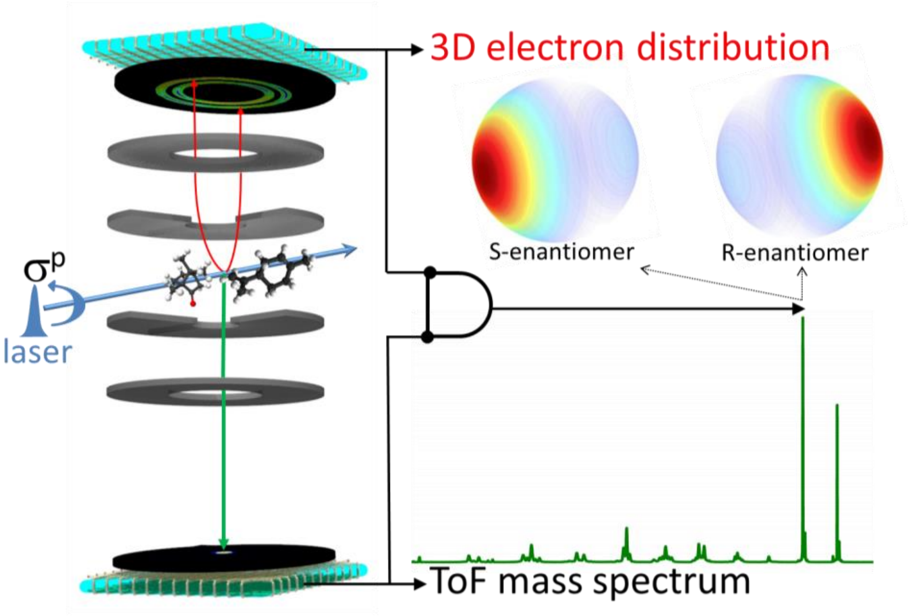

Figure: Concept of Mass-Selective PhotoElectron Circular Dichroism.

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High-throughput on-line monitoring of microorganism of relevance in food technology by PTR-ToF-MS

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Microorganisms have been widely used in food technology since millennia for the fermentation of raw matrices (cereal, grape must, milk, meat) to obtain fermented food (beer, bread, wine, yogurt, cheese, sausage). Their metabolisms affect many properties of fermented food, with a noteworthy influence on the content of volatile compounds (VOCs) affecting perceived sensory quality. VOCs concentrations are not only function of quality and quantity of the microorganisms used as starter cultures to promote fermentation, but also depend on their interaction with food matrices and with the technological regimen applied. Therefore a rapid and non-invasive screening of microorganism volatolomes is of outmost relevance in the evaluation and selection of microbial strains for the food industry and in the optimization of the associated food bioprocesses.

FEM developed a Proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) based set-up [1] which showed promising results in monitoring food bioprocess applications of different microbial strains. Particularly challenging is the monitoring of alcoholic fermentation due to the primary ion depletion and formation of ethanol clusters caused by high concentrations of ethanol in the sample headspace [2]. Two different methodological approaches have been used to overcome the issue with a high ethanol emission during yeast growth such as inert gas dilution as described in Makhoul et al [2] and fast GC demonstrated by Romano et al [3].

In this contribution, we report three paradigmatic cases study on the potential of the method in terms of high-throughput, sensitivity, reproducibility, and stability: 1) the characterization of yeast volatilome of six different *Saccharomyces cerevisiae* strains (4 meiotic segregants of a natural strain and 2 laboratory strains) inoculated onto a solid YPD medium and monitored for 11 days every 4 hours [4]; 2) the exploration of the interactions among two *S. cerevisiae* strains and two non-*Saccharomyces* strains in the grape juice/must environment, in order to optimize VOCs content in the final product; 3) the monitoring of lactic fermentation in yoghurt preparation driven by 4 different yogurt commercial starter cultures inoculated in milk [5].

The described set-up allows the on-line high-throughput screening of volatilome associated with microorganisms development in food matrices. Moreover it might be helpful in validation of new hypothesis in basic science, identification of strain specific features and new metabolic pathways, discrimination of genetically similar strains, and quality control.

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Mathematical Modeling for Breath Gas Analysis

Julian King, ZF Friedrichshafen

"Dedicated to Karl Unterkofler, on the occasion of his 60th birthday."

As a biochemical probe, volatile organic compounds (VOCs) in exhaled breath are unique in the sense that they can provide both *non-invasive* and *continuous* information on the metabolic state of an individual. This information might fruitfully be used for dynamic assessments of normal physiological function (e.g., during stress challenges or in an intra-operative setting), pharmacodynamics (drug testing), and environmental exposure (e.g., in occupational health).

Within this framework, we focus on *real-time* measurements of VOCs during distinct physiological regimes such as rest, exercise, and sleep. An experimental setup combining breath-by-breath analyses using quadrupole and time-of-flight proton transfer reaction mass spectrometry (PTR-TOF-MS) with data reflecting the behavior of major hemodynamic and respiratory variables is presented. Furthermore, a methodology for complementing VOC profiles obtained by PTR-MS with simultaneous SPME/GC-MS measurements is outlined.

Building on these experimental findings, the second part of the talk will be devoted to a modeling study of the physiological flow of acetone, isoprene, and methane, which rank among the most notable compounds studied in the context of breath gas analysis. In particular, it will be examplified how mechanistic modeling approaches can provide a conceptual framework for identifying and understanding the key relationships governing the breath behavior of VOCs, thereby facilitating experiment design and helping to avoid misinterpretations of empirical results. The results discussed are intended a first step towards employing breath gas analysis as a tool for monitoring general exhalation, storage, transport, and biotransformation processes associated with volatile organic compounds *in vivo*.

[^{13}C]-Dextromethorphan breath test for evaluation of CYP2D6 enzyme activity in patients with breast cancer taking tamoxifen

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Abstract:

The phenotype ^{13}C-dextromethorphan breath test (DM-BT) was used to evaluate the activity of the enzyme cytochrome P450 2D6 (CYP2D6) in comparison to its genotype.

A multi center open label study with 103 female breast cancer patients was conducted over 3 years in an institutional review board (IRB) approved study in Tyrol and Vorarlberg. The study population consisted of two arms – before (arm 1) and at least 90 days after Tamoxifen therapy (arm 1+2). The DM-BT was administered to each arm 1 patient on their first visit to ascertain the baseline CYP2D6 enzyme activity using the biomarker $^{13}CO_2$ in breath. After ongoing Tamoxifen therapy for at least 90 days second DM-BT was performed on arm 1 and the only one DM-BT for arm 2 patients. Mouth saliva swabs were taken to determine their CYP2D6 genotype.

DM-BT was administered to all 103 patients. Only 71 patients whose genotype and activity scores was available were eligible for data analysis.

Phenotype-genotype correlation resulted in 37 of 71 non-poor metabolizers (PM) whereas 3 of 5 PMs by phenotype correlated with PMs by genotype.

In the current study, we found the CYP2D6 phenotype correlates better with the N-Desmethyl tamoxifen/Endoxifen ratio than endoxifen especially if steady state for endoxifen has not been reached.

The DM-BT can rapidly (50 min) evaluate CYP2D6 phenotype and enzyme activity especially when potent inhibitors of CYP2D6 are taken as concomitant drugs resulting in phenoconversion which the genetic test cannot detect.

Investigation of ion chemistry of glyoxal

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Abstract

Glyoxal (m.w. 58 g/mol) is a highly reactive molecule associated with some basic biological processes. Glyoxal is associated with oxidation stress [1], with catalytic reaction formed basic organic molecules in inorganic environment [2] and is ono of the products of oxidation of anthropogenic and biogenic volitale organic compounds (VOC) [3]. Previous PTR-MS study [4] showed significant dependence of the *m/z* 59 product abundance on humidity. Moreover, a signal at *m/z* 31 (probably protonated formaldeyhde CH_2OH^+) resulting from glyoxal reaction was observed, which correlated with the system's humidity.

In present investigation, SIFT-MS experiment [5] was used for investigation of ion-molcular interaction of glyoxal with H_3O^+, NO^+ and $O_2^{\bullet+}$ reagent ions at variable humidities. In advance, we provided injection of water through helium carrier gas, avoiding interaction of water with glyoxal in the sampling system. For H_3O^+ reagent ion we observed behaviour similar to PTR-MS study [4]. Adittionally, humidity dependence for glyoxal water clusters were obtained. For NO^+ and $O_2^{\bullet+}$ reagent ions we observed ion formation comparable to previous SIFT investigations [6-7]; formation of $OC(H)C(H)O(NO)^+$ ion and $OC(H)C(H)O^{\bullet+}$ ion from NO^+ and $O_2^{\bullet+}$ reagent ions, respectivly. Humidity dependence was estimated for these ions as well.

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Presence of water clusters in SCIMS

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Abstract

Ion chemistry that takes place inside a flow or a drift tube reactor of a soft chemical ionization mass spectrometer, SCIMS, is highly sensitive to presence of water vapour in carrier gas. This effect is very prominent especially in a proton transfer reaction system initiated by the H_3O^+ reagent ion. Presence of water molecules inside the flow/drift tube leads to a series of association reactions and to formation of $(H_2O)_N{*}H_3O^+$ clusters [1]. Effective evaluation of absolute concentrations of investigated analytes strongly depends on accuracy of the evaluation of rate constants and on information about relative ratio of the reagent ions. This evaluation can be done in a controlled laboratory environment, but operation of instruments in regular environment as for a clinical or environmental application can't satisfy this condition. It is thus important to understand the dynamic influence of humidity on results of analyses using SCIMS techniques.

Here we present a comparison of experimentally obtained data and theoretical calculation of expected concentrations of reacting ions with respect to concentration of neutral water molecules inside the flow/drift tube reactor containing He carrier gas. Experimental data were provided by investigation of acetone using SIFT-MS [2] and investigation of several alcohols using SIFDT-MS [3] systems. The experimental results are compared with a reaction system kinetics model based on numerical solution of a complete set of differential equations describing the ion chemistry using the classical Runge-Kutta method. Based on a number of free parameters, only approximate analysis was obtained and the uncertainty of the rate coefficients determined using modelling of complex experimental data remains to be estimated.

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Separation of monoterpenes using fast-GC and SIFT-MS techniques

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Abstract

Present study describes a combination of fast-GC with SIFT-MS analytical technique for selective analyses of biogenic volatile organic compounds (BVOCs) that play a critical role in atmospheric chemistry; they are associated with surface ozone production and secondary aerosol formation [1, 2]. Proper estimation of their concentration is necessary for the purpose of atmospheric photochemical modelling. Currently, the accurate amount of non-methane biogenic emissions, represented mainly by methanol, isoprene and monoterpenes which belong to the most important plant volatiles (present at concentrations below 1 part per billion by volume, ppbv), is uncertain due to a lack of selective and robust in-situ analytical methods and instruments.

SIFT-MS is able to quantify wide range of volatile organic compounds simultaneously in real time, anyway selectivity is still limited; only the total concentration of monoterpene isomers can be quantified. Thus, more traditional method of gas chromatography (GC) has to be employed. Because GC is time consuming we have used fast-GC [3, 4] coupled to SIFT-MS [5]. For investigation, we used 5 m long metal MXT-1 column (0.28mm x 0.1 um) used previously [6] with resistivity ~4.2 Ω/m requiring heating current below 5 A. A separate investigation of elution times combined with ion chemistry [7] for eight the most abundant plant monoterpene isomers (α-pinene, β-pinene, Camphene, Myrcene, 3-carene, R-limonene, α-terpinene and γ-terpinene) were used for successful separation and identification of monoterpenes contained in an artificially prepared monoterpene mixture as well as in several biological samples.

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Acknowledgment

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Proton Transfer Reaction – Mass Spectrometry and its Applications to Homeland Security: detection of Illicit Drugs

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Proton Transfer Reaction Mass Spectrometry (PTR-MS) is an analytical technique for the detection of trace chemical compounds in complex environments through soft chemical ionisation useful in many fields including food sciences, health sciences, environmental sciences and homeland security.

For security applications PTR-MS has been successfully used to detect chemical warfare agents, explosives and narcotics. Within this area the rapid and sensitive detection of trace quantities of compounds without initial separation is crucial in security areas such as ports, airports and, in general, in locations where people and goods circulate in outstanding quantities. Although highly sensitive, PTR-MS is based on the volatility of the targeted chemicals, which can raise difficulties when searching for low vapour compounds.

To amend this, a Thermal Desorption Unit (TDU) in conjunction with a PTR-MS instrument can be used. It has recently been applied to the detection of explosives [1] and in this study we demonstrate the application of a TDU for the on-line detection of trace quantities of the most widely used societal drugs: cocaine, heroin, morphine, ecstasy, and codeine, the reactions of which with H_3O^+ at just one reduced electric field, 120 Td , have already been reported [2].

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INVESTIGATIONS OF VOCS PRESENT IN BREATH USING PTR-MS: PRELIMINARY STUDIES OF KETONES, ISOPRENE AND ANAESTHETICS

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The need for a non-invasive clinical diagnostics has grown over the past years. Breath research is gaining an important role in this field. More than 500 volatile organic compounds (VOCs) in breath can provide us with a wide variety of biomarkers. Most of these compounds are present in very low concentrations (sub parts per billion), therefore finding a sensitive instrument for analysing breath samples is crucial. Proton transfer reaction mass spectrometry (PTR-MS) has proven its qualities in many research fields including breath research.[1,2] Its high sensitivity for VOCs, easy or usually no sample preparation and if used correctly, high selectivity, provide us with a strong analytical tool. Although PTR-MS usually uses H_3O^+ as a reagent ion (RI), it can also be used in modes to produce different RIs, e.g. O_2^+ and NO^+, which react with VOCs of interest providing the reactions are exothermic.[3]

In our work we are aiming to create a database of VOCs present in breath and their reactions with RIs, the product ions of which could serve as biomarkers for diseases. Although predominantly focused on PTR-MS we have also investigated a number of compounds using ion mobility spectrometer (IMS) and gas chromatography mass spectrometer (GC-MS).

The investigation with the ketones is a major collaborative project involving 3 ESRs from 3 organisations. We measured and analysed fragmentation patterns while changing the reduced electric field for 21 compounds.[4] A fast GC was coupled to the PTR-MS in order to separate isobaric compounds, which can have often completely different origins in the human body and therefore can be found in the breath. Some of these substances were measured also with different RIs and different humidity conditions, to provide us with an even wider database to allow ease of identification under different conditions.

Another important study undertaken was the analysis and comparison of breath samples from almost 100 healthy participants as a part of study in cooperation with Institute für Ernährungsphysiologie und Physiologische Chemie in Wien. In this study we focused on the quantification of isoprene and its dependence on diet.

In addition to investigating endogenous breath compounds, we have begun to investigate important exogenous compounds in breath. To date we have focused on the anaesthetics, isoflurane and sevoflurane. The question to address is how long an anaesthetic remains in the body following surgery? Investigations will include length of surgery, dose and patients' details (e.g. age). Initial studies have been undertaken to determine the product ions following reaction with H_3O^+, in order to determine which ions should be monitored. Detailed studies of product ions as a function of reduced electric field will be presented.

In future research we plan to measure other ketones with all available RIs, continue research with anaesthetics and later move this research to investigating the breath of patients after surgeries for a period of several days.

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IMS and IMS-oaTOFMS detection of VOC's

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In this work we are going present our application of ion mobility spectrometry (IMS) and IMS-orthogonal acceleration Time of Flight mass spectrometry (IMS-oa-TOF MS) [1] for detection of VOC's with reactant ions (RI) generated by corona discharge (CD). Among other we are going to present the resent results regarding chemical ionisation (CI) of phthalates in positive polarity of IMS. In this mode $H_3O^+(H_2O)_n$ clusters interacts with phthalate molecules and formation of different types of molecular ions including protonated parent ions, H_3O^+ adduct ions and their dimmers was observed. We have observed that the ionisation probability of phthalates depends on the gas temperature of the IMS instrument.

The CD IMS is very efficient instrument for detection of the phthalates. We have achieved limits of detection down to parts per trillion (ppt) range. The ion composition of the ions formed was studies using the IMS-oaTOF instrument. In the synchronised mode the 2 dimensional spectra allowed us to assign the ions detected in the mass spectrometer to the IMS peaks. The high sensitivity of IMS for detection of VOC's makes it a suitable instrument for their monitoring and detection.

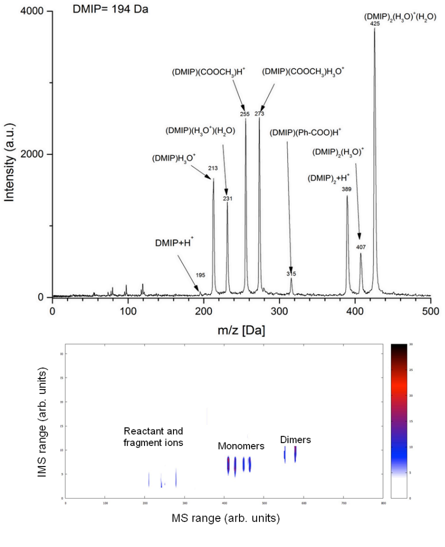

Figure 1. Spectra of DMIP phthalate i) mass spectrum (upper panel) ii) 2 dimensional IMS-MS map.

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Characterisation of the semi-volatile component of Dissolved Organic Matter by Thermal Desorption – PTR-ToF-MS

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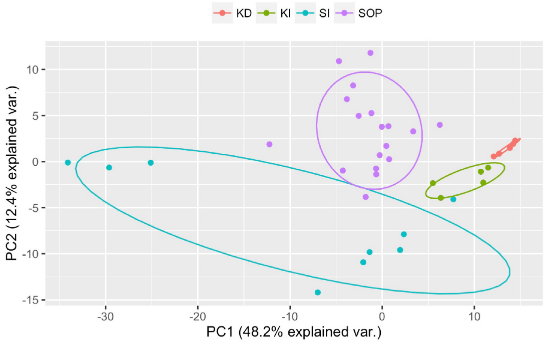
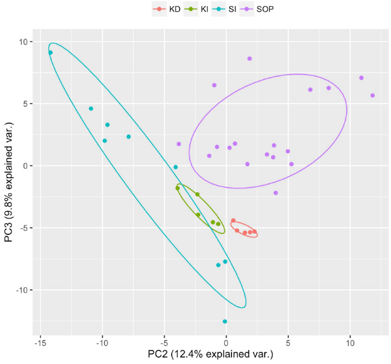
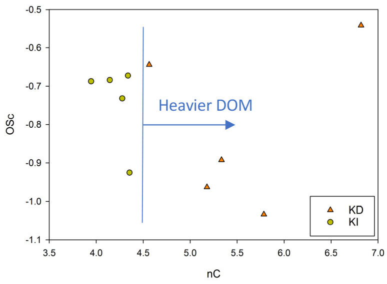
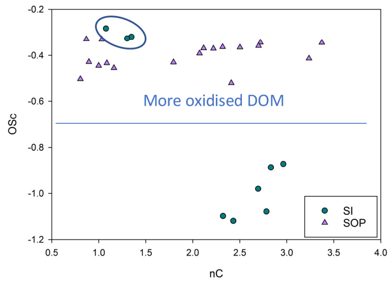
Abstract

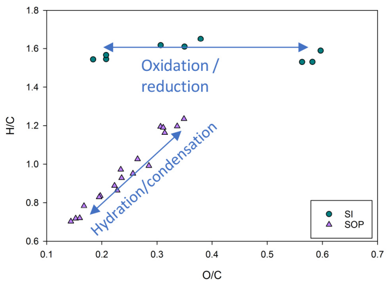
Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is a sensitive, soft ionisation method suitable for qualitative and quantitative analysis of volatile and semi-volatile organic vapours. PTR-MS is used for various environmental applications including monitoring of volatile organic compounds (VOCs) emitted from natural and anthropogenic sources, chemical composition measurements of aerosols, etc. Here we apply thermal desorption PTR-MS for the first time to characterise the chemical composition of dissolved organic matter (DOM). We developed a clean, low-pressure evaporation/sublimation system to remove water from samples and coupled it to a custom-made thermal desorption unit to introduce the samples to the PTR-MS. Using this system, we analysed waters from intact (KI) and degraded (KD) peat swamp forest of Kalimantan, Indonesian Borneo, and an oil palm plantation (SOP) and natural forest (SI) in Sarawak, Malaysian Borneo. We detected more than 250 organic ions from these samples and principal component analysis allowed clear separation of the different sample origins based on the composition of organic compounds. The method is sensitive, reproducible, and provides a new and comparatively cheap tool for a rapid characterisation of water and soil DOM.











Charge transfer reactions in helium droplets: Theory and experiment

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Helium droplets provide experimental means to investigate atoms and molecules at very low temperature. Helium droplets have an equilibrium temperature of 0.37 K and most atoms and molecules are picked up and transferred to the centre of a helium droplet upon collision which leads to rapid cooling of the dopant. With decreasing temperature, the number of quantum states with significant occupation probabilities decreases substantially. In addition, working at low temperature makes it possible to form chemical species which would be unstable at room temperature.

An important issue in mass spectrometric investigations of doped helium droplets is the process of charge transfer upon electron impact. In case of electron energies above 24.6 eV, i.e. the ionization energy of helium, resonant charge hopping from the surface of the helium droplet towards the dopant takes place. In case the charge gets close to the dopant within a certain amount of steps it will ionize the dopant, otherwise He_2^+ will be formed [1]. For electron energies below 24.6 eV an electron bubble is formed inside large enough helium droplets which can move towards the dopant and eventually interact with it. However, for electron energies around 22 eV it was experimentally shown that atomic and molecular helium anions can be formed [2]. In this presentation we discuss the formation of these anionic species on ground of quantum chemical calculations and discuss their implications for charge transfer processes within helium droplets [3,4]. We will show that both single and double charge transfer reactions from the atomic helium anion to embedded molecules in helium droplets can occur [5].

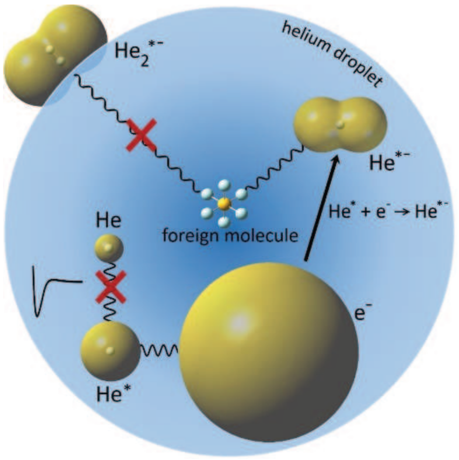

Fig.1 Properties of atomic and molecular helium anions in helium droplets.

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Enhancement of Compound Selectivity Using a Radio Frequency Ion-Funnel Proton Transfer Reaction Mass Spectrometer: Improved Specificity for Explosive Compounds

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A key issue with any analytical system based on mass spectrometry with no initial separation of compounds is to have a high level of confidence in chemical assignment. This is particularly true for areas of security, such as airports, and recent terrorist attacks have highlighted the need for reliable analytical instrumentation.

Proton transfer reaction mass spectrometry is a useful technology for these purposes because the chances of false positives are small owing to the use of a mass spectrometric analysis. However, the detection of an ion at a given m/z for an explosive does not guarantee that that explosive is present. There is still some ambiguity associated with any chemical assignment owing to the presence of isobaric compounds and, depending on mass resolution, ions with the same nominal m/z. In this study we describe how for the first time the use of a Radio Frequency Ion-Funnel (RFIF) in the reaction region (drift tube) of a proton transfer reaction–time-of flight– mass spectrometer (PTR-ToF-MS) can be used to enhance specificity by manipulating the ion–molecule chemistry through collisional induced processes. Results for trinitrotoluene, dinitrotoluenes, and nitrotoluenes are presented to demonstrate the advantages of this new RFIF-PTR-ToF-MS for analytical chemical purposes.

CORONA DISCHARGE ION MOBILITY SPECTROMETRY AS A GOOD TECHNIQUE FOR PHTHALATES DETECTION.

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In recent years phthalates have been accused of showing negative impact on human health. Breast cancer in females or mental and motor development in children can be caused by long term exposure on phthalates. So it is important to have a good tool to detect them rapidly even at very low concentrations. In many laboratories research groups have been studying phthalates using different methods. The most common technique that phthalate esters were investigated is gas chromatography coupled with mass spectrometry (GC-MS), [1][2]. Recently Midey et al. present some results where high-performance ion mobility spectrometry with direct electrospray ionization (ESI-HPIMS) was used to detect some phthalates [3].

In our laboratory five phthalates have been investigated using corona discharge ion mobility spectrometry (CD-IMS) at atmospheric pressure. Benzyl butyl phthalate, diphenyl isophthalate, diphenyl phthalate, ditridecyl phthalate and dimethyl isophthalate have been measured and limits of detection (LOD's) were determined. Chemicals which we have studied are characterized by very low vapour pressures, for example vapour pressure of benzyl butyl phthalate is $2 \cdot 10^{-4}$ Pa [4], which means that these are non-volatile compounds and detection in gas phase can be difficult. For that particular phthalates LOD obtained in our laboratory is tens of ppt.

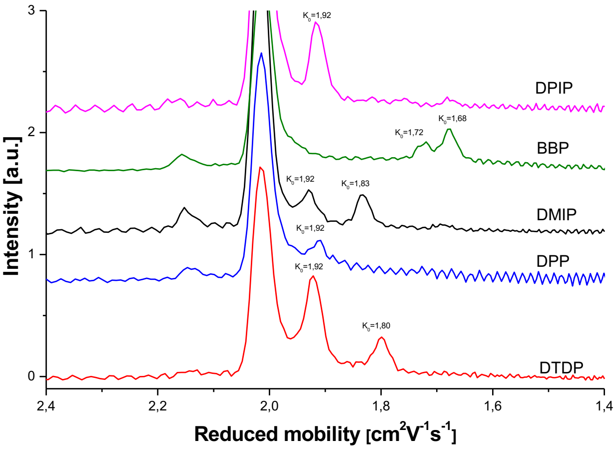

Fig. 1. IMS spectra for investigated phthalates.

Experiments that we have performed in our laboratory and obtained results show clearly that atmospheric pressure discharges in our case corona discharge applied in ion mobility spectrometers can be used to detect phthalates at very low concentration.

Acknowledgment

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- MaSa TECH, s.r.o.

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Monitoring of selected volatile organic compounds released by hidden humans using gas chromatography ion mobility spectrometry (GC-IMS)

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The trafficking and smuggling of people to Europe have reached epidemic proportions in recent years. This does not only put a major strain on European resources, but puts at risk the health and lives of the people being trafficked or smuggled. Of particular concern is the increasing trend of smuggling migrants hidden inside shipping containers or trucks containing different cargos. In this context, the early detection and interception of smuggled people is of particular importance in terms of saving migrants from life-threatening situations. Consequently, there is a growing demand for a portable security device for the rapid and non-intrusive monitoring of cargoes to detect any people hiding inside cargo containers. A number of recent studies by us suggest that volatile chemical fingerprinting associated with emissions from humans has the potential to detect stowaways hidden inside shipping containers or trucks.

The talk will be devoted to the application of ion mobility spectrometry coupled with gas chromatography (GC-IMS) to determine and monitor volatile organic compounds (VOCs) released by human body under conditions that mimic entrapment and the evaluation of this technique for real life scenarios. The study involved a cohort of subjects (n=11) enclosed in a body plethysmography chamber for a period of 2 hours. During the first hour of the experiment only the skin-borne VOCs were targeted and the subjects inhaled and exhaled the outside air. During the second hour, subjects exhaled directly into the chamber interior, while still inhaling outside air. Thus, during this second-phase both breath- and skin-borne volatiles accumulated in the chamber. VOCs were monitored using a high resolution IMS coupled to a gas chromatograph developed at Leibniz Universität, Hannover. Coupling of the IMS with a GC column considerably improves selectivity while preserving high sensitivity without the necessity for sample pre-concentration.

More than 80 VOC-related ion mobility peaks were found in the air of the chamber. 35 of these corresponded to human presence in the chamber. Of these 17 were reliably identified and quantified, including 7 aldehydes (acrolein, 2-methylpropanal, 3-methylbutanal, 2-ethacrolein, n-hexanal, n-heptanal, benzaldehyde), 3 ketones (acetone, 2-pentanone, 4-methyl-2-pentanone), 5 esters (ethyl formate, ethyl propionate, vinyl butyrate, butyl acetate, ethyl isovalerate), one alcohol (2-methyl-1-propanol) and one organic acid (acetic acid). The mean concentration values of the majority of these volatiles were in the range of 1-10 ppbv. In conclusion we have demonstrated that a fast GC-IMS has considerable potential for use as a portable field detector for human presence. Furthermore, the findings of this study are expected to enhance our understanding of the origin and fate of VOCs emitted by human organism under stressful conditions.

CF_3^+ and CF_2H^+ as reagents in CI-MS: VOCs and Breath

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Real time measurements of volatile organic chemistry compounds (VOCs) using chemical ionization mass spectrometry has many applications in different fields such as breath analysis [1]. This work has explored the application of CF_3^+ as precursor in chemical ionisation reaction time-of-flight mass spectrometry (CIR-TOF-MS). Experiments have been conducted to explore the quantitative determination of n-alkanes (C_2-C_6) using CF_3^+ / O_2 as precursors. The result show that ethane, propane and n-butane with CF_3^+ show small signs of fragmentation at both values of E/N (51 and 99 Td). The predominant peaks of ethane, propane and n-butane are at m/z 19, 43 and 57 with relative abundances >90%. Pentane and hexane gave more fragmentation particularly at 99 Td. The results of these alkanes with O_2^+ showed higher fragmentation (see Fig 1) [2]. The approach has been expanded to target VOCs selected for their abundance in breath and environmental samples. The results with CF_4 shows that there is a competitive between CF_3^+ and H_3O^+ as precursors with VOCs and results generally in these types: $R.CF_3^+$, $R.CF_2^+$, $(R\text{-}1)^+$ and R^+ which might produce by combination, elimination of water/OH^- and hydrogenation. Meanwhile, the type of products of O_2 with VOCs are R^+, $(R\text{-}1)^+$ and $R.O_2^+$. The results of breath samples show that some compounds which released from smokers might identified such as acetonitrile.

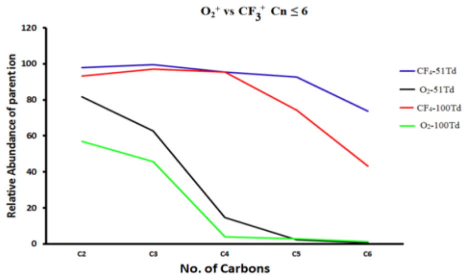

Figure 1: Relative abundance of M^+ for $C_{n<6}$ alkanes with CF_3^+ and O_2^+.

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The good, the bad and the aged: quality control of anhydrous milk fat through Proton Transfer Reaction Mass Spectrometry

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Abstract: PTR-MS (Proton Transfer Reaction Mass Spectrometry) is an accurate, highly sensitive, direct-injection technique that allows for the rapid characterization of food products and for the monitoring of processes in food science and agro-industry, without any pre-treatment [1]. In the last years, the importance of this technology in food research has increased quickly and it has been applied to address different issues as monitoring food and drink quality, monitoring volatile emission changes during time (e.g. shelf life) and rapid classification of food samples according, e.g., to geographical origin [2].

This study aims at verifying whether headspace analysis through PTR-MS, coupled with a time of flight detector and a multipurpose sampler can correctly classify anhydrous milk fat (AMF) samples according to classes defined by sensory analysis. 39 samples were divided in three classes (OK, BAD, AGED) according to sensory evaluation by 7 to 12 trained panelists (OK, BAD) and thermal treatment (AGED). All the samples were then measured through PTR-ToF-MS in five replicates for a total of about 200 measurements. Measurements were performed in an automated way using a multipurpose GC automatic sampler (Gerstel GmbH, Mulheim am Ruhr, Germany) connected to the inlet of a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria). PTR-MS data were then extracted [3, 4] and multivariate analysis was applied. After peak masses selection through statistical comparison (1-way ANOVA with Boneferroni correction, p.value <0.01) with blanks, principal component analysis (PCA) was conducted. The analysis lead to a clear separation of the three different classes. PLS analysis was then performed to see to build a discrimination model. By using raw data (without mass selection) all the samples were correctly classified with the exception of only one sample.
This pilot study indicate that PTR-ToF-MS can be implemented as a rapid and efficient tool for anhydrous milk fat quality control in agroindustry.

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Analysis of gasoline and diesel exhaust using Selective-Reagent-Ionization Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (SRI-PTR-TOFMS)

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PTR-TOFMS is a sensitive, unselective soft chemical ionization technique to monitor trace concentrations of volatile organic compounds (VOCs) on-line and in real-time. The SRI option increases the selectivity by providing additional reagent ions (O_2^+ and NO^+) and thus further reaction channels. This allows separation of isomers and charging of compounds, which are not ionizable by H_3O^+.

The composition of traffic emissions, including their effects to human health and climate, is one of the applications that are receiving increasing attention in recent years. Car exhaust is composed of a very complex chemical matrix. Well known constituents are CO_2, NO_x and particulates. Furthermore it consists of a variety of volatile and, in the case of diesel exhausts, intermediate volatile organic compounds (IVOC). IVOCs are defined as compounds with a saturation vapor pressure between $1.33*10^{-4}$ to $1.33*10^{-1}$ hPa. This pressure range corresponds to C_{12} - C_{18} compounds. Because of the low vapor pressure IVOCs are effective condensing material for secondary organic aerosol (SOA) formation. Emitted compounds (i.e. primary emissions) can either directly affect human health (e.g. carcinogenic aromatic and polycyclic aromatic hydrocarbons) or by secondary processes in the atmosphere. The emissions are highly dynamic by nature and strongly depend on engine load, fuel type and exhaust gas treatment. Hence PTR-TOFMS is a very well suited method to study car exhaust.

Here we present first results of a measurement campaign during June 2017 at IFSTTAR (Bron, France) studying primary emissions of EURO5 gas and diesel fueled cars. Cars were driven according to Worldwide harmonized Light vehicles Test Cycle (WLTC). The WLTC consists of a realistic acceleration and deacceleration profile for urban, rural and motorway driving. Over 30 cycles have been measured and analyzed with SRI-PTR-TOFMS for a better characterization of emission profiles.

FP was supported by the EU Marie Curie ITN IMPACT (GA 674911).

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Real time calibration of aliphatic amines

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Aliphatic amines such as methylamine, dimethylamine and trimethylamine represent an important class of compounds that can be found in biological fluids and environmental samples often at trace levels. The measurement and quantification of aliphatic amines is difficult to perform due to their polar, basic and hydrogen-bonding properties which make reliable calibrations complicated.

In our study, we addressed the problem of real time calibrations for methylamine, dimethylamine and trimethylamine. A PTR-Tof-MS 8000 was used for real time measurements. Respect to off-line analytical techniques such as GC-MS, PTR-Tof-MS offers an interesting alternative for the monitoring of fast changes in concentration profiles, avoiding losses and contaminations of samples associated to sample storage and pre-concentration. The gaseous standards at different concentrations were prepared in Tedlar bags by dilution with pure nitrogen. The PTR conditions were optimized in terms of inlet flow, inlet temperature, drift temperature, drift pressure and electric field. Each bag was measured for 10 minutes and linear regression analysis was carried out plotting the concentrations versus the PTR response at each minute of measurement.

The correlation coefficients ranged from 0.8831 to 0.9977. LODs and LOQs were determined according to the standard S/N definition. The LODs ranged from 0.8 ppbV to 27 ppbV, LOQs ranged from 1.4 ppb to 52 ppb.

The results suggest that the method can be used for the identification of aliphatic amines in human breath.

A systemic view on exhaled volatile organic compounds in mice: a promising new level in the world of pan-omics

Jan Rozman and Martin Kistler

Mutant mouse lines are important model systems in biomedical research. They allow the in-depth investigation of gene functions linked to human disease, detection of early biomarkers for disease diagnosis, and developing and testing of new strategies for treatment of disease. Here, the success of both large-scale screening projects aiming to identify so far unknown gene functions as well as mechanistic studies to decipher the molecular basis of disease depends on a broad and systemic understanding of pathological alterations on different organismic levels. This systemic view on physiological functions comprises data from genomics and different levels of phenomics including proteomics and metabolomics.

Improvements in the area of "*breathomics*" could add a new dimension to this world of pan-omics by mapping patterns of exhaled volatile organic compounds to metabolic pathways and disease related gene functions. To achieve this aim, animal models and especially mouse mutant lines need to be included. In the Energy Metabolism & Diabetes Lab of the German Mouse Clinic, we developed and implemented breath analysis as a new non-invasive method to characterize metabolic functions in mutant mice. We will present the current state regarding general approaches, methodological aspects, and media-links of exhaled VOCs. In addition, we will discuss possible future directions of breath analysis in mouse models with a metabolic phenotype.

Electron driven reactions in doped He nanodroplets

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Pickup of atoms or molecules by He nanodroplets leads to the formation of cold complexes with unique properties. Long-range electrostatic interaction leads to the orientation of polar molecules prior to the attachment to the dopant cluster, which forms dipolar chains [1,2]. The binding energy of a newly adsorbed particle is completely dissipated into the surrounding heat bath (isothermal at 0.37K) before the next particle arrives. Thereby these metastable dipole-oriented chains are stabilized. Ionization or electronic excitation of the surrounding He matrix leads to ionization of the dopant via charge transfer (from He^+ or He^{*-}) or Penning ionization or [3,4,5]. All processes leading to the formation of cations are highly exothermic with most dopants. Competition between fragmentation and efficient cooling by the surrounding He matrix determines the resulting product ions. Ions from doped He nanodroplets are often extremely cold and thus less prone to vibrationally induced fragmentation as recently demonstrated for multiply-charged alkali cluster cations [6]. Often a few He atoms may stay with dopant ions which provides often interesting structural information [7,8] or the possibility to use them as taggants for messenger type spectroscopy [9].
Particularly for anions soft ionization can be achieved utilizing doped He nanodropets and even stabilization of reaction intermediates has been observed [10].

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Applications of Soft Chemical Ionisation Mass Spectrometry for Clinical Breath Analysis

Rostock **M**edical: **B**reath research, **A**nalytics & **T**echnologies
https://anaesthesie.med.uni-rostock.de/forschung/atemgasanalytik-rombat/
Prof. Dr. med. Dipl. Chem. Jochen Schubert
Vice Director of Department of Anaesthesiology and Intensive Care
University Medical Center Rostock

This lecture describes a series of clinical studies carried out by means of proton transfer reaction mass spectrometry (PTR-MS and PTR-ToF-MS).

Time and place of breath sampling can have a distinct impact onto exhaled substance concentrations and may easily override endogenous effects. Concentrations of breath biomarkers – but also those of typical contaminants – change rapidly and in a pronounced way within minutes in the clinical environment. Punctual breath sampling or simple subtraction of background air is not sufficient to account for this problem.

There are immediate effects of human physiological changes on VOC exhalations in breath. The extent of different physiological effects on VOCs depend on the origin and physico-chemical properties and distribution kinetics of the compounds. Changes in breathing patterns (e.g. breath holding or FEV maneuvers) and changes in body positions had profound effects on exhaled VOC concentrations. Physiology induced changes in exhaled VOC compositions returned to initial baseline within a certain timeframe. Breathing route induced changes depended on respiratory parameters, oral and nasal cavity exposers and physico-chemical characters of the compounds.

Volatile breath constituents such as acetone and ammonia have been linked to dextrose, fat, and protein metabolism. Non-invasive breath analysis, therefore, may be used for metabolic monitoring, identification of fuel sources actually used for energy production and determination of the anaerobic threshold (AT). Exhaled concentrations of acetone, ammonia, and isoprene were determined in 21 healthy volunteers under controlled ergometric exercise. In parallel, spiro-ergometric parameters (VO_2, VCO_2, respiratory rate and minute ventilation) and hemodynamic data such as heart rate were recorded. AT was determined from serum lactate, by means of respiratory exchange rate and by means of exhaled acetone concentrations. Exhaled acetone concentrations mirrored exercise

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Experimentelle Anästhesiologie

ROSTOCK MEDICAL
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induced changes of dextrose metabolism and lipolysis. Bland–Altman statistics showed good agreement between lactate threshold, respiratory compensation point (RCP), and determination of AT by means of exhaled acetone. Exhaled ammonia concentration seemed to be linked to protein metabolism and changes of pH under exercise. Isoprene concentrations showed a close correlation to cardiac output and minute ventilation. Breath biomarkers represent a promising alternative for metabolic monitoring under exercise as they can be determined noninvasively and continuously. In addition, these markers may add complementary information on biochemistry, energy production and fuel consumption.

Breath analysis could offer a non-invasive means of intravenous drug monitoring if robust correlations between drug concentrations in breath and blood could be established. Effects of changes in pulmonary blood flow resulting in a decreased cardiac output (CO) and effects of dobutamine administration resulting in an increased CO on propofol breath concentrations and on the correlation between propofol blood and breath concentrations were investigated in seven acutely instrumented pigs. Increasing cardiac output led to a deterioration of the relationship between breath and blood propofol concentrations. Decreasing pulmonary blood flow and cardiac output through banding of the pulmonary artery did not significantly affect the relationship between propofol breath and blood concentrations. Estimation of propofol blood concentrations from exhaled alveolar concentrations seems possible even when cardiac output is decreased. Increases in cardiac output preclude prediction of blood propofol concentration from exhaled concentrations.

In critically ill patients, VOC analysis may be used to gain complimentary information beyond global clinical parameters. This seems especially attractive in mechanically ventilated patients frequently suffering from impairment of gas exchange. Exhaled VOC concentrations varied with recruitment induced changes in minute ventilation and cardiac output. Ammonia exhalation depended on blood pH. The improvement in dorsal lung ventilation during recruitment ranged from 9%to 110%. Correlations between exhaled concentrations of acetone, isoprene, benzene sevoflurane and improvement in regional ventilation during recruitment were observed. Extent and quality of these correlations depended on physico-chemical properties of the VOCs. Combination of continuous real-time breath analysis and Electro Impedance Tomography (EIT) revealed correlations between exhaled VOC concentrations and distribution of ventilation. This setup enabled immediate recognition of physiological and therapeutic effects in ICU patients.

Monitoring metabolic adaptation to chronic kidney disease (CKD) early in the time course of the disease is challenging. As a non-invasive technique, analysis of exhaled breath profiles is especially attractive in children. Ammonia accumulated already in CKD stage 1, whereas alterations of isoprene (linked to cholesterol metabolism), pentanal and heptanal (linked to oxidative stress) concentrations were detectable in the breath of patients with CKD stage 2 to 4. Only weak associations between serum creatinine and exhaled VOCs were noted. Non-invasive breath testing may help to understand basic mechanisms and metabolic adaptation accompanying progression of CKD. These results support the current notion that metabolic adaptation occurs early during the time course of CKD.

Strong points of Soft Chemical Ionization Mass Spectrometry are non-invasiveness, continuous analyses without any burden to the patient and unlimited repeatability. These features can be used to address important basic issues in clinical breath analysis such as influence of physiology onto results. In addition, this technique provides optimal conditions for longitudinal and cross sectional studies exploring short and even long term changes in breath biomarkers.

"Ion Mobility Spectrometry vs Mass Spectrometry: How ambient ionisation changes the game!"

Dr Peter Hickey and Dr Patrick Sears
Dstl Fort Halstead, Sevenoaks, Kent, UK

The Defence and Security sector requires technology to be able to detect threat explosives and related materials, in order to protect people and infrastructure. Most commercially available trace explosives detection systems are based on ion mobility spectrometry. Ion mobility spectrometry technology has remained largely unchanged since its introduction to the marketplace, over 40 years ago. Despite the improvements in resolution and therefore selectivity and sensitivity that mass spectrometry appears to offer, it has, to date, not made significant inroads for explosive detection applications.

In this talk, we will discuss the challenges of deploying mass spectrometry, as well as the benefits provided by ion mobility spectrometry that have enabled it to remain the dominant technology. Recent advances in ambient ionisation provide an opportunity to enhance the performance of both ion mobility spectrometry and mass spectrometry for the detection of explosives. A review of ambient ionisation techniques that could be applied to this field will be discussed, and the potential for these advances to change the status quo in favour of mass spectrometry will be highlighted.

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Chemical Ionization of Linear Ketones by H_3O^+, NO^+, O_2^+ in the Drift Tube

Anatolii Spesyvyi[1], Patrik Španěl[1], David Smith[2].

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Ion-molecule reactions of ketones with H_3O^+, NO^+, O_2^+ ions are well studied under the thermal conditions using Selected Ion Flow Tube Mass Spectrometry. Further development of the soft chemical ionizations mass spectrometry, SCIMS, techniques involves the introduction of the electric field into the flow tube, thus expanding it to the drift tube. Energy of the ion-molecule interaction in the drift tube depends on the electric field strength. Presented work shows influence of this energy on the product ions distributions and rate coefficients of reactions of H_3O^+, NO^+, O_2^+ with acetone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone and 2-octanone. Experiments were provided with Selected Ion Flow Drift Tube instrument using helium as carrier gas. This enabled to reach interaction energies up to 0.5 eV between reagent ion and neutral ketone of interest. Results of the study can be useful for the SCIMS techniques improvement and for discussions about the nature of ketones chemical ionization processes.

Selected Ion Flow Tube Mass Spectrometry, SIFT-MS: from plasma physics via analytical chemistry to medicine

Patrik Španěl.

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The need for rapid and accurate measurement of trace concentrations of compounds present in air and human breath has led to construction of specialised soft chemical ionization mass spectrometers based on the Selected Ion Flow Tube Mass Spectrometry, SIFT-MS (Fig. 1). It is possible currently to analyse vapours of volatile organic compounds and other gases including ammoniac, hydrogen sulphide or hydrogen cyanide present in concentrations as low as a part per billion by volume (ppbv). The lecture will outline to construction and principle of operation of these instruments and also present interesting examples of their use including clinical breath analysis. A specific focus will be given to aspects of this technique that are not often discussed in research literature from plasma processes in the ion source via ion chemistry issues influencing quantification accuracy to interesting medical case studies.

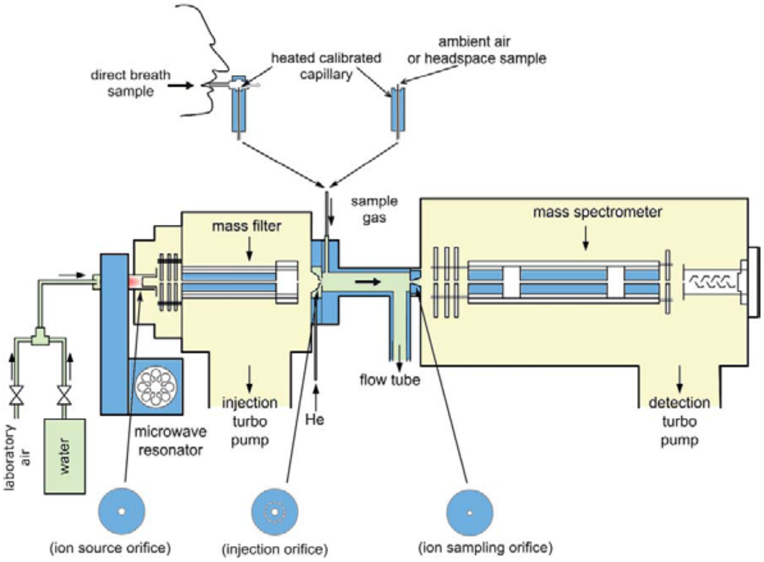

Fig. 1 A schematic diagram of the *Profile 3* SIFT-MS instrument showing the microwave discharge ion source, injection mass filter and the three metal discs to which ion current can be measured and which support the orifices through which (i) ions pass from the ion source into the injection mass filter, (ii) mass selected reagent ions enter the flow tube reactor, (iii) reagent and analyte ions pass from the carrier gas/reactor into the analytical quadrupole mass spectrometer. Both direct breath sampling in the instrument and sampling from ambient air, samples in bags or liquid headspace can be achieved

Overview of Marine Air Reactivity during AQABA (Air Quality and Climate Change in the Arabian Basin) Campaign June-August 2017.

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Abstract

From June to August 2017, the ship campaign AQABA (air quality and climate change in the Arabian basin) was conducted starting from Southern France, proceeding through the Suez Canal, rounding Arabian Peninsula into the Arabian Gulf and on to Kuwait, then returning along the same route. Air quality in this region is highly influenced by dust events, emissions from marine transportation, from the petroleum industry. The combination of strong sunlight and heavy trace gas loadings leads to highly active photochemistry, producing ozone and secondary organic aerosol both of which are important to human health and regional radiative balance. We continuously measured the total reactivity of the air presented by all gas phase species to the atmosphere´s primary oxidant OH as well as volatile organic compounds (VOCs) using two Proton Transfer Reaction Mass Spectrometers (PTR-MS) throughout the campaign. From the preliminary results obtained so far, the lowest levels of total OH reactivity (below 5 s^{-1}) were found in the Arabian Sea under south easterly wind conditions, representing the clean air. Much higher reactivity (20 to 50 s^{-1}) was measured in the Arabian/Persian Gulf and Suez Canal, which is probably related to emissions from oilrigs and passing ships. Most of the major VOCs (e.g. acetone, benzene) showed similar spatial trends to the OH reactivity but dimethyl sulfide (DMS) was observed to be much higher in a region of upwelling off the coast of Djibouti. To our knowledge, these are the first total OH reactivity and VOCs measurements made in this region. The results can provide new insights into the atmospheric processes in the Middle East, to assess the impact of oil industry related emissions and improve the model predictions related to air quality.

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Exploring Air Chemistry with PTR-MS

Jonathan Williams, Max Plank Institut, Mainz

The field of atmospheric chemistry has been revolutionized with the arrival of on-line mass spectrometric techniques such as Proton Transfer Reaction Mass Spectrometry. New soft ionization approaches have allowed scientists to “see” new atmospherically important species and to monitor them in real time. By operating such instruments all over the world on planes, ships, in cities and in forests we have gained new insights into the emission, chemistry and removal of airborne chemicals, in particular volatile organic compounds (VOC). Example data from such field expeditions will be shown and discussed in this talk. In addition to the measurement of individual compounds, the PTR-MS instrument has been also used to measure total atmospheric reactivity, so that relative importance of the individual species in air oxidation chemistry can be assessed. Recently, by measuring VOC and OH reactivity with PTR-MS in the pristine Amazon rainforest and from downtown Beijing, we have show clearly how the local air chemistry impacts ozone.

Are the polar seas a net source or sink of Oxygenated Volatile Organic compounds (OVOCs)?

Measurements of a variety of OVOCs (alcohols, ketones, aldehydes) in the sea water and air of the high Canadian Arctic using PTR-MS coupled to segmented flow coil equilibrator (SFCE)

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6. University of East Anglia, United Kingdom

Acetone, acetaldehyde and methanol consume 80% of the OH radicals in the maritime atmosphere[1]. Owing to the high solubility and in situ production of Oxygenated Volatile Organic Compounds (OVOCs), the oceans have an enormous potential to act as a source or a sink. Additionally, their reactivity, ubiquity, high solubility and presence at ppb or nM levels makes detection challenging. Previous atmospheric measurements of these compounds in the high Arctic could not explain observed concentrations by air mass transport alone pointing towards local sources[2].

We have developed a segmented flow coil equilibrator (fig 1, left) which allows for continuous extraction of these compounds from the waterside. The segmented flow coil equilibrator was coupled to PTR-MS and deployed on an expedition in the high Canadian Arctic on board the ice breaker NGCC Amundsen (fig 2, right). The PTR-MS was switching between underway water and air measurement of these compounds to compute the flux. Additionally, depth profiles of the concentration of OVOCs in the water column will be presented.

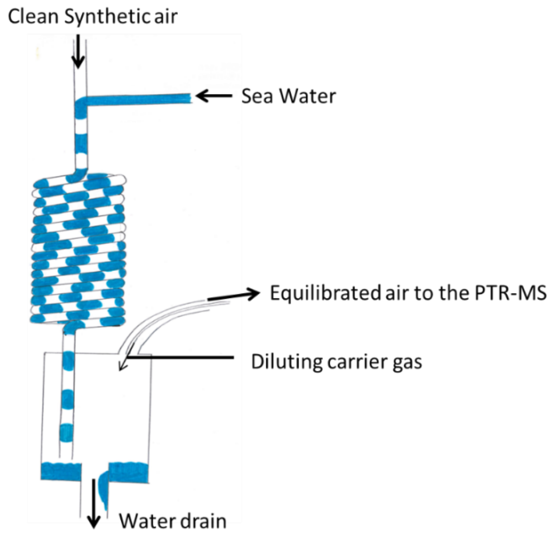

Figure 1: **Left:** Segmented flow coil equilibrator; Sea water and clean synthetic air mix in a 10m long coil submerged in a water bath. While travelling through the coil, the water and the carrier gas equilibrate with the neighbouring section of air. The equilibrated carrier gas is analysed by PTR-MS. **Right:** Deployment on board the ice breaker NGCC Amundsen and alteration between waterside and airside measurements of OVOCs.

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PTR-MS STUDY OF KEY VOCS FROM MANUKA HONEY OF VARIOUS ANTI-BACTERIAL STRENGTHS – DR. S. ZAFAR

CO-AUTHORS: Dr. C. Mayew, Dr. G. Mehena.

ABSTRACT

We have studied the volatiles from Manuka honey using Proton Transfer Reaction Mass Spectrometry. This study was conducted to ascertain if there are any correlations between the Unique Manuka Factor (UMF) and volatile concentrations. UMF is the labelling used to highlight the calculated amount of antibacterial content of Manuka honey, which in comparison to other honeys is superior. Our hypothesis was that the Manuka volatile content associated specifically with Manuka antibacterial should increase linearly with increasing UMF value.

One important volatile organic compound, methylglyoxal (MGO), is associated with the unique antibacterial properties of Manuka honey, which is rated according to the UMF. Our key finding is that headspace levels of MGO (or any other volatile) do not correlate to the UMF. The reason for the lack of any correlation could be certain factors affecting the honey and these will be reported in the presentation.

Although headspace analysis was not found to be useful for determining UMF, the detection of MGO and other volatiles directly associated with floral origin, such as methyl syringate, dihydroxyacetone and dihydroxyacetone-phosphate provide a unique fingerprint for Manuka honey. Included in the fingerprint is the detection of volatiles resulting from reactions during the making of honey, namely 4-Methoxyacetophenone and 4-Methoxybenzoic acid, thereby providing a means for authentication of the product.

Study of gas-phase ion molecular reactions relevant to the atmosphere of Mars

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Theoretical models of the chemical kinetics of the ionosphere of Mars are highly dependent on the precision of the rates of the reactions of ambient ions with neutral gases. To provide data at the required temperature range, the newly built VT-SIFT instrument includes a novel temperature variable flow tube and temperature regulation system was used to study temperature dependence of N_2^+ + O_2 and NO_2^- + CO_2 reactions at temperatures in the range of 220 – 300 K.

The charge transfer reaction of positive N_2^+ ion with oxygen measured over the temperature range 220 – 300 K (figure 1):

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2 \qquad (1)$$

is not considered as relevant to Martian atmosphere. Despite of abundance of O_2^+ ions gas and neutral oxygen, N_2^+ ions is not dominant in the ionosphere of Mars [Haidler et al. 2011]. However it was used to estimate the absolute error of rate coefficient measurements using this new VT-SIFT instrument. Measured rate coefficients are in good coincidence with previously published data obtained using different techniques.

Anions CO_3^- and NO_2^- are abundant in negative ion spectra of the troposphere of Mars, while carbon dioxide is dominant gas of Martian atmosphere [Haidler et al. 2011]. Measured rate of the reaction of O^- transfer (figure 2)

$$NO_2^- + CO_2 \rightarrow CO_3^- + NO \qquad (2)$$

is very slow compare to typical Langevin values in the range of 225 – 300 K. The rate coefficient of the reaction has significant negative temperature dependence: $k = (2.4 \pm 0.6)\cdot10^{-14}$ cm^{3}s^{-1} at 300 ± 2 K and $k = (7.9 \pm 1.9)\cdot10^{-14}$ cm^{3}s^{-1} at 224 ± 4 K.

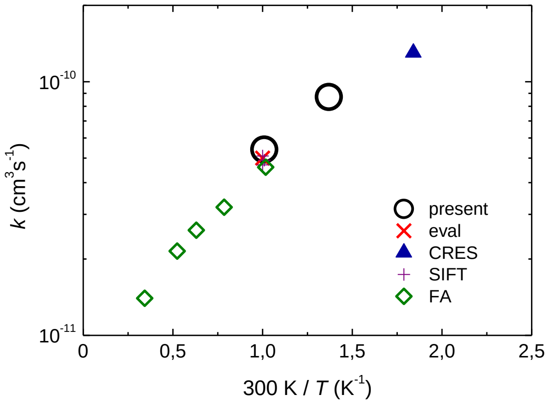

Figure 1 Measurements of the N_2^+ + O_2 charge transfer reaction rate coefficient in the range of temperatures 220 – 300 K (black circle markers) compared to previous measurements [Lindinger et al., 1974], [Gaucherel et al., 1986], [Adams et al., 1980].

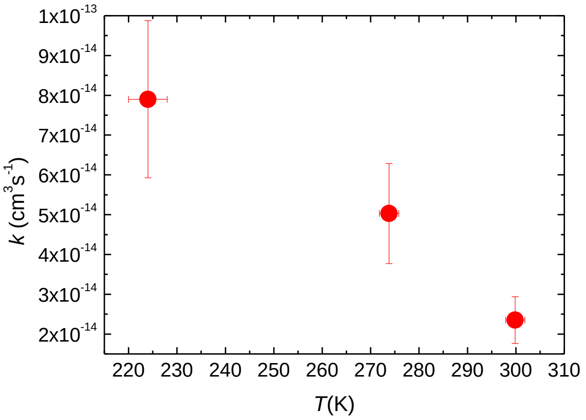

Figure 2 Measurements of the temperature dependence of the reaction of NO_2^- anions with carbon dioxide neutral gas over the range of 225 – 300 K. Number density of neutral helium carrier gas in the flow tube is order of magnitude of 10^{-16} cm^{-3}.

Acknowledgments

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