1st International Conference on Proton Transfer Reaction
Mass Spectrometry and Its Applications

Contributions

Editors:
Armin Hansel
Tilmann Märk

Institut für Ionenphysik
der Universität Innsbruck
Technikerstrasse 25
6020 Innsbruck, Austria

Igls / Innsbruck, Austria
January 18 – 23, 2003
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Foreword

Ten years ago we built the first Proton Transfer Reaction Mass Spectrometer instrument (PTR-MS) in Werner Lindinger’s Laboratory at the Institut für Ionenphysik of the University of Innsbruck. This technique combines the idea of chemical ionization introduced by Munson and Field in 1966 with the swarm technique invented by Ferguson and his colleagues in the early 70’s. PTR-MS uses preferentially proton transfer reactions to chemically ionize volatile organic compounds present in gaseous media e.g. in air. With this technique a variety of organic species in complex matrices can be monitored on-line with detections limits as low as a few pptv. In 1998 we founded a company (Ionicon Analytik GmbH) to provide this technique to a growing user community as a fast VOC sensor. Now more than 50 instruments are used by many research groups and companies around the world applying this technique in various fields.

The goal of this first PTR-MS conference is to bring together active scientists and technologists from both academia and industry involved in real-world mass spectrometric measurements of VOCs. The intent for this meeting is to promote discussions and the free exchange of ideas across disciplines such as environmental sciences, food technology and medicine.

On the occasion of this Conference we want to hand over to Werner’s family a special issue of the International Journal of Mass Spectrometry to honor the late Professor Werner Lindinger, who died in an tragic accident two years ago.

Armin Hansel
This Volume is dedicated to the memory of the late

Professor Werner LINDINGER
A Homage to Werner Lindinger

The scientific community lost a great friend and highly esteemed colleague with the tragic drowning of Werner Lindinger in Hawaii on Feb. 16, 2001.

Born in 1944 in a small town in Tirol (Brixlegg) Werner Lindinger studied, after finishing high school in Kufstein, physics (1963-1972) at the Leopold Franzens Universität in Innsbruck, Austria. He started his academic career already during his study years by joining in 1967 the newly founded Institut für Atomphysik as a “wissenschaftliche Hilfskraft”. In his thesis supervised by the head of this institute (Prof. Maximilian Pahl) Werner Lindinger measured the presence of ions in the negative glow of a hollow cathode with a mass spectrometer and from this on mass spectrometry and ions became the subject of his scientific life. Already towards the end of his thesis he showed his great scientific talent by finding a way to analyse the measured radial ion densities in a hollow cathode discharge and to deduce corresponding reaction rate constants for the underlying ion molecule reactions occurring in the hollow cathode discharge thus leading to a first acclaimed publication (W.Lindinger, Reaction rate constants in steady-state hollow-cathode discharges: Ar + H₂O reactions, Phys.Rev. A7 (1973) 328).

Following his Ph.D. degree obtained 1972 in Innsbruck, Werner initiated his professional career as a Max Kade Foundation post doctoral fellow in the NOAA Aeronomy Lab in Boulder from Oct. 1973 to Sept. 1975. His considerable talent and exceptional energy led to an extremely productive period in Boulder. He rigorously exploited the newly developed flowing afterglow technology for the measurement of thermal and low energy ion-molecule interactions, ion mobilities and ion reactions with neutral molecules. This outstanding research activity earned him in 1976 at an exceptional young age after his return to Innsbruck in 1975 the Fritz Kohlrausch prize, the most prestigious award the Austrian Physical Society can hand out. His warm and outreaching personality led to the formation of many deep friendships in Boulder at NOAA and JILA, many persisting actively throughout his life.

Upon his return to the Science Faculty at Innsbruck he was one of the leaders instrumental in developing an atomic and ion physics program at the Institut für Atomphysik involving the construction of a new flow drift tube and investigating in detail the dependence
of ion molecule reactions on temperature and energy. After obtaining in 1977 the Habilitation for the subject “experimental atomic physics” he quickly achieved international recognition leading also to a professorship in 1978 at the Institut für Experimentalphysik. In 1987 he was elected head of the newly founded Institut für Ionenphysik in Innsbruck. After constructing in these years one of the first selected ion flow tubes (SIFT, see W. Lindinger et al., “Investigations of ion-molecule-reactions using a drift tube with separated ion source, Int.J.Mass Spectr.Ion.Phys., 30 (1979) 251) important contributions were made by Werner and his group to ion-molecule reaction kinetics and a variety of ion-molecule interaction processes as well as original contributions to thermochemistry (Phys.Rev.Lett., 52 (1984) 2084; Phys.Rev.Lett., 54 (1985) 540). A notable example of these achievements is a series of studies on molecular ion vibrational quenching in neutral collisions. The first publication of a systematic study on ion vibrational relaxation was in 1983 an Innsbruck publication in J. Chem. Phys., 97 (1983) 553, the most recent a publication in 2000 again in J. Chem. Phys., 112 (2000) 731.

In recent year Lindinger’s interests shifted leading to the application of ion flow systems to super sensitive detection (in the ppt region) of trace gases in an on-line, real time manner (with time resolutions below 1s) by first introducing charge exchange ionisation and later on the proton transfer reaction mass spectrometry (PTR-MS) technique. Lindinger and colleagues pioneered its use in a variety of applications in medicine and food analyses, as well as highly time-resolved studies of the emissions from vegetation and biomass burning to the atmosphere. Starting with a close collaboration between Werner’s group and the Max Planck Institut für Chemie in Mainz many research groups around the world are now applying this technique for studies of biosphere-atmosphere interactions using instruments built in a company (Ionicon Analytik GmbH) founded by Werner Lindinger and colleagues in 1998. At the time of his death he was in Hawaii for the purpose of installing his PTR-MS instrument at the NOAA Clean Air Baseline Station on the volcanic Mauna Loa mountain.

Lindinger was together with the late Prof. Franz Howorka one of the founders 25 years ago of the popular „Symposium on Atomic and Surface Physics (SASP)“ held every two years, often in Tyrol but also in other European countries. In recognition of this and also for his outstanding scientific achievements in the field of ion-molecule reactions Werner received in 1996 the SASP Schrödinger Award and the Golden Medal of the Comenius University, Bratislava. His great scientific achievement was also recognised in 1997 by the receipt of
Austria’s highest science award, the Erwin-Schrödinger Prize of the Austrian Academy of Science.

In addition to his prolific publication record, Werner lectured widely in Europe and the US for many years, being a guest professor at the University of Trento and the University of Utah, Salt Lake City and authored numerous contributed and invited reviews (see the most recent one entitled “Ion-molecule reactions” in Adv. In Atomic, Molecular and Optical Physics, 43 (2000) 243).

The concept to produce a special issue of the International Journal of Mass Spectrometry to honour the late Werner Lindinger arose spontaneously on both sides of the Atlantic, in Innsbruck and at the Gaseous Ion Chemistry Gordon Conference in Ventura, California, attended by both the U. S. and European senior Editors of this journal. Two of undersigned (Jean Futrell and Tilmann Märk) were invited to serve as guest editors of this special edition to be handed over to Werner’s family on the occasion of this 1st International Conference on Proton Transfer Reaction Mass Spectrometry in Igls/Innsbruck, Austria in January, 2003. The number and quality of the papers (see the contents section of Int. J. Mass Spectrometry 223/224 (2003) are themselves a testimony to the high esteem in which Werner Lindinger was held by his colleagues and friends and the breadth of Werner’s scientific interests. Although each author in this IJMS volume has his/her own story to tell about Werner we (the editors of this volume) think it fitting to add here some personal remarks from the perspectives of both a personal, close colleague and coworker in Innsbruck and an occasional coworker from abroad.

One of us (JHF) joined the Institut for the academic year 1980-81 as a Fulbright Professor and got to know Werner and the other Founding Fathers, Tilmann and the late Professor Franz Howorka—ironically also a victim of accidental death in 1990. Their hallmarks on the Institut remain clearly visible and it was a special privilege to know all of them in the early pioneering years. The strength of the interaction led to annual visits for several years and Innsbruck remains a prime European destination for my scientific and personal travels. It is a further testimony that younger staff now taking leadership roles continue the same traditions of excellence in research and collaborations with a very broad range of scientists that pulls visitors to Innsbruck. Werner considered Utah, Delaware, and Washington, close enough to Boulder (and to his ranch in Durango, Colorado) to include us in
his itinerary. Shortly before his death the Pacific Northwest National Laboratory had initiated the purchase of a PTR-MS instrument from his company, Ionicon Analytik GmbH. We were anticipating his close involvement with our atmospheric chemistry group involving static testing of urban environments and airborne sampling by our research aircraft that were carried forward but without his guidance.

For the other of us (TDM) Werner was a great companion for 40 years, starting in 1962 together as students of physics at the University of Innsbruck, and joining in 1968 together the newly founded Institut für Atomphysik and then pursuing our academic careers in parallel at the University of Innsbruck until his untimely death. Werner impressed me from the beginning by three character traits which made working together with him in an institute a rewarding experience, strong willpower, loyal friendship and deep insight into science. Most important of all he always had time or took time to have a coffee and to discuss things which mattered.

Werner’s interest were broad and varied. In addition to his research and teaching he had a lively appreciation of art and music. He was a vigorous person physically. Like many (most) Tyroleans he was an accomplished skier. He was an avid hiker and a regular tennis player. In recent years he became a serious equestrian, riding in two African safaris. Werner’s extraordinary joy of living made his friendship a rewarding and memorable experience. He will be sorely missed. We lost a dear friend, a generous colleague and an extraordinary scientist. Werner’s over-riding characteristic, manifested in so many ways, was his great zest for living. He truly thought he could do anything he chose to do. He was almost correct.

Paul Crutzen, Mainz
Eldon Ferguson, Boulder
Jean Futrell, Richland
Tilmann Märk, Innsbruck
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- **mass range:** 1 - 512 amu
- **measuring time:** 2 ms – 60 s/amu
- **response time:** < 200 ms
- **measuring range:** 10ppt – 10 ppm
- **linearity:** 10ppt – 5 ppm
- **inlet flow:** adjustable 15 – 200 sccm
- **inlet temperature:** adjustable 30 – 70 °C
- **reaction chamber temp.:** adjustable 40 – 80 °C
- **weight:** 130kg
- **power:** 230V/115V 700Watt
- **physical dimensions LxHxW [cm]:** 78 x 86 x 55
Compact PTR-MS

A Compact Proton-Transfer-Reaction Mass-Spectrometer (PTR-MS) is now available for use in Food Research, Medicine, and Environmental Trace Gas Monitoring. The real-time method uses $\text{H}_3\text{O}^+$ primary ions, which perform mostly non-dissociative proton transfer reactions with Volatile Organic Compounds (VOCs) present in air. Organic trace gases such as carbonyls, alcohols, aldehydes, BTX-compounds and many others are monitored within seconds with a detection limit of 1 ppbv. The fully computer controlled instrument weighs only 120 pounds and measures 22 x 25 x 17 inches.
Features of the instrument:

- Provides absolute concentrations for formaldehyde in gas-phase and liquid-phase.
- Fully automated continuous operation using micro controller.
- Automated calibration using internal HCHO permeation source or liquid HCHO standards.
- Ranges liquid phase measurement: 0 to 30.0 µg/l (free programmable) 0 to 300 µg/l, 0 to 1.5 mg/l.
- Ranges gas phase measurement: 0 to 20.0 ppbV (free programmable) 0 to 200 ppbV, 0 to 2.0 ppmV.
- HCHO gas-phase detection limit of < 50 ppt.
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- Detection limit: < 1.5 ppb at 1 s  
  < 0.8 ppb at 10 s
- Rise- and fall time (10 to 90 %) < 0.1 s
- Low weight (24 Volt DC-air craft version available) < 22 kg
- Rugged and simple to use.
- RS232- and LAN- interface to external PC
Elemente
des Erfolgs

Gase und Know-how:
Nutzen für viele Branchen
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SANTO ALI, PHILIPPE POLLION, CHRISTIAN LINDINGER, CHAHAN YERETZIAN
1. Opening Lecture
The powerful PTR-MS analytical technique can trace its origin back to the Flowing Afterglow technique developed in 1964 in the Boulder Laboratories of the National Bureau of Standards, subsequently renamed the National Oceanographic and Atmospheric Administration.

The present paper is a brief summary and overview of the early FA development and some of the early applications. The FA revolutionized the measurement of thermal energy ion-molecule reactions as a consequence of its vastly enhanced versatility, resulting essentially from the separation of ion and neutral reactant introduction. All prior techniques at that time involved ionization of gas mixtures whose limitation had restricted the known I-M rate constants to ~100 reactions of very limited type. The FA increased this number by orders of magnitude in a short time and extended the range of reactions studied to charge-transfer reactions the first associative detachment of negative ions, reactions of ions with O, N, H, atoms, O3, N2O5 etc.

The motivation of the Boulder group was the delineation of the ion chemistry of the ionosphere, for which none of the IM reactions had been determined at that time and not all of which had been identified. This was accomplished in a few years by the FA co-developers, Art Schmeltekopf and Fred Fehsenfeld and a number of very productive Post-Docs, several of whom became leaders in IM reaction studies in their home countries, including Lindinger (Austria), Rowe (France), Bohme (Canada), Adams (England) and two exceptional PhD students, McFarland who built the first Flow Drift tube for his thesis and Viggiano who has had an outstandingly productive career at the Air Force Lab near Boston.

The mechanism by which proton hydrates are produced as the dominant positive ions in the D-region and upper stratosphere was discovered. The negative ion chemistry of the atmosphere was determined prior to any atmospheric measurements.

Analytical applications included the first gas phase sulfuric acid concentration measurements in the stratosphere by Arnold in Heidelberg, the discovery and concentration of acetonitrile in the stratosphere, also by Arnold, and the highest altitude determination of water vapor concentration (~95 km) utilizing the Si+ loss scheme proposed and measured in Boulder,
Si$^+$ + H$_2$O → SiOH$^+$ + H, applied again to meteorically derived ions measured in the atmosphere by Arnold.

The first systematic study of proton transfer (as a function of energy) was carried out by Werner Lindinger in Boulder and ultimately led to Werner's development of the PTR-MS analytical technique in Innsbruck, perhaps the most useful application of all for ion flow systems.
2. Invited Lectures
2.1. Environmental Science and Technology
Field Measurements with PTR-MS under different photochemical pollution situations

Dommen J. ¹, Steinbacher M. ¹, Prévôt A.S.H. ¹, A. Neftel²

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
²Swiss Federal Research Station for Agroecology and Agriculture, CH-8046 Zürich, Switzerland

ABSTRACT

The temperature stabilisation of the inlet system and the drift tube of the proton-transfer-reaction mass spectrometer has strongly improved the stability of the blank values. The humidity dependence of benzene was negligible under our operating conditions. The response of the PTR-MS (mass 31) to formaldehyde (HCHO) is only 20%. A comparison of HCHO measurements with the Hantzsch fluorimetry technique and the PTR-MS showed large discrepancies probably due to contribution of other species like methylhydroperoxide or fragmentation. Mass 107 correlated well with GC measurements of C2-benzenes in winter, but exhibited large deviations in a summer field campaign.

1. Introduction

Volatile organic compounds (VOC) play an important role in the formation of ozone and other photooxidants. In comparison to most of the common techniques (e.g. the sampling on cartridges with an off-line analysis) the proton-transfer-reaction mass spectrometer (PTR-MS) has the potential to determine a large variety of VOCs at a high time resolution in combination with a low detection limit. Until now we participated in 3 field campaigns with a PTR-MS. This allowed us to compare PTR-MS measurements with measurements from conventional instruments.

A first field campaign took place in the city of Bern, Switzerland in March 2001, close to a main road. Furthermore the PTR-MS was used within the scope of the CHAPOP (Characterization of High Alpine Pollution Plumes) project in August 2001. The CHAPOP field campaign was performed in the Leventina valley in Southern Switzerland, through which the transalpine traffic via the Gotthard route runs. One aim of CHAPOP is to quantify the mass exchange and transport of polluted air between the atmospheric boundary layer and the lower free troposphere. In summer 2002 the FORMAT (Formaldehyde as a tracer of photooxidation in the Troposphere) campaign was performed in the Lombardy region in Northern Italy to study formaldehyde formation under heavily polluted conditions. The presentation will give an overview of some experiences and results with the PTR-MS.

2. Instrumentation

We operated two PTR-MS instruments of IONICON. In the first two campaigns we used an older version of the instruments that had a drift tube of 9.5 cm length and 5 cm diameter, while the newer version had a drift tube of 9.25 cm length and 1.4 cm diameter. Furthermore, in the new instrument the inlet system and the drift tube were temperature stabilised to 50 °C. The old system had an inlet made of PFA while the new one comprises a Silcosteel® inlet.

A commercial Airmotec HC1010 gas chromatograph was used to measure hydrocarbons speciated between C4 (hydrocarbons containing four carbon atoms) and C10 (Konrad and Volz-Thomas, 2000). Sample air is aspirated through adsorption tubes containing Carbopack B and Carbosieve III. The adsorption tubes are installed on a revolving cylinder. While a sample is collected on the first tube the second tube is desorbed and the third tube is purged with hydrogen. The instrument operated in a mode to obtain concentrations averaged over 30 minutes.
Formaldehyde (HCHO) was continuously detected with the Hantzsch method as described by Kelly and Fortune, (1994). Formaldehyde is collected in a glass coil scrubber. The Hantzsch reaction is used to produce a fluorescent derivative in a heated reaction coil, which is detected by fluorimetry.

3. Measurements

3.1. Temperature stability of the instrument

In field experiments environmental conditions are usually less stable and comfortable compared to measurements in the laboratory. During the CHAPOP campaign our field laboratory experienced a large temperature variation, which also influenced the PTR-MS instrument. The zero level of the instrument was determined with the help of an activated charcoal cartridge. Figure 1a shows the strong dependence of our blank values from temperature as taken by the older instrument. While the temperature varies by about 10°C the blank values of the masses 79 (benzene), 107 (C2-benzenes) and 121 (C3-benzenes) changed by 0.15-0.25 ppb. During the FORMAT campaign similar diurnal temperature variations were occurring in the measurement container. However, the new instrument showed no dependency on the temperature (Fig. 1b). It is also noticed that the new instrument shows a much lower level of the blank values. Figure 1b shows a slowly decreasing signal of the blank values over the course of the five days. A new electron multiplier detector had to be installed before the start of the measurements. In the beginning a higher signal is obtained which then decreases a few days to a constant signal level.

![Figure 1: Temperature dependence of the blank values during the CHAPOP field campaign with the old instrument (a) and during FORMAT with the new instrument (b).](image)

3.2. Humidity dependence measurement

Warneke et al. (2001) showed a humidity dependence of benzene and toluene, which they explain as a function of the cluster ion distribution. They used the instrument with a drift tube pressure of 2.5 mbar and an electric field of 65 V/cm. We operated the PTR-MS with a drift tube pressure of 2.1 mbar and an electric field of 62 V/cm and did not observe a humidity dependence for benzene (Fig. 2). A sensitivity of 49 cps/ppb was obtained for benzene at 4.2 \(10^6\) cps of primary ions.

![Figure 2: Calibration curve of benzene in air at five different relative humidity values.](image)
3.3 Formaldehyde measurements

We compared mass 31 of the PTR-MS (which corresponds to protonated formaldehyde) with measurements of a Hantzsch instrument. Different concentrations of HCHO were produced by dilution of a diffusion source. The PTR-MS showed only 20% of the Hantzsch signal (Figure 3a). However, the simultaneous measurement of laboratory air yielded quite a different result. Now, the PTR-MS signal was only 40% lower than the Hantzsch instrument. A comparison of 5 days of measurements during the CHAPOP campaign is presented in Figure 3b. A typical diurnal variation of the mixing ratios is seen the first four sunny days during high photochemical reactivity. The last two days were cloudy and concentrations stayed rather low. The two instruments show often a similar behavior. Generally the Hantzsch instrument has higher values than the PTR-MS, but there are also a few cases when even the PTR-MS is higher. The ratio of the Hantzsch signal to mass 31 varies between 0.5 and 2.5. Since the mass 31 signal is generally much higher than expected from the laboratory comparisons, other species like methylhydroperoxide or fragments of other species must contribute to it. We found no correlation of the signal ratio of the two instruments with photochemical activity or hydrocarbons. It seems not to be possible to quantify HCHO concentrations with the PTR-MS under ambient conditions.

![Figure 3a](image1.png)  
![Figure 3b](image2.png)

Figure 3: a) Comparison of different gaseous HCHO concentrations with a Hantzsch instrument and the PTR-MS. b) HCHO concentrations measured with the Hantzsch instrument and mass 31 of the PTR-MS during a field campaign from 26 August to 01 September 2001 in the Leventina valley.

3.4 C2-benzenes

Measurements of C2-benzenes and mass 107 during the winter campaign in Bern are presented in Figure 4. We found a good correlation between the GC measurements (sum of o-, m-, p-xylene) and mass 107 of the PTR-MS. However, the PTR-MS showed consistently lower values by 30%. Both instruments were calibrated to the same benzene standard. Reasons for the discrepancy could be e.g. a too high reaction rate constant, which is used to calculate the concentration or some coeluting species in the GC.
Figure 4: Xylene-measurements by GC and PTR-MS in Bern in March 2001

Measurements during the summer campaign in the Leventina exhibited a different picture. Mass 107 was always higher than the GC measurements especially during the sunny period in the beginning. This suggests, that a photochemical product might be contributing to mass 107. One of these could be benzaldehyde, which is formed from the oxidation of toluene. We calculated the difference between the concentration given by mass 107 and the C2-benzenes from the GC. This difference concentration X shows a rather good correlation with benzene. Thus X may contain a primary pollutant being emitted concurrent with benzene. Traffic exhaust is the main source of benzene and a major species with mass 107 from that seems questionable. On the other hand toluene and other substituted benzenes, which are emitted together with benzene, can be oxidized leading to benzaldehyde and other oxidized species of mass 107. This could finally lead to the observed correlation with benzene.

Figure 5: Measurement of aromatics with the GC and of mass 107 with PTR-MS during the CHAPOP summer campaign (left). Difference between mass 107 and C2-benzenes from the GC compared to benzene.

4. References


VOC Measurements of Urban Air in the Mexico City Metropolitan Area using the Proton Transfer Reaction Mass Spectrometer

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ABSTRACT
The Proton Transfer Reaction Mass Spectrometer (PTR-MS) because of its high sensitivity and fast time response is finding increased application in the study of the atmospheric chemistry of volatile organic compounds (VOC’s) in polluted urban air masses. In February 2002, a PTR-MS instrument was deployed as part of the Collaborative Field Measurement of Photochemical Air Quality of the Mexico City Metropolitan Area campaign and the results of that study are presented. Because of the complex nature of the highly polluted urban air mass in Mexico City, characterization of the PTR-MS responses which only provide ion mass information requires additional information. Using known chemical inventories for the Mexico City Metropolitan Area (MCMA) along with co-located canister sampling data analysed by gas chromatography–flame ionization detector (GC-FID) and the full mass spectral scans from the PTR-MS allowed seven individual compounds or classes of compounds to be identified and quantitated. These compounds include methanol, acetaldehyde, C$_3$H$_6$O (acetone + propanal), benzene, toluene, C$_8$H$_{10}$ (C2-benzenes) and C$_9$H$_{12}$ (C3-benzenes) and constitute approximately 50% of the total PTR-MS response. Potential spectral interferences have been considered and evaluated for each compound or class of compounds and only the benzene measurement appears to suffer significantly from interference from other unrelated compounds. Sample concentrations derived from the PTR-MS ion intensity measurements are compared to collocated canister samples analysed by GC-FID and to post campaign calibration experiments. Good quantitative agreement between the PTR-MS and GC-FID methods was observed for the aromatic compounds. However, post campaign experiments using calibrated gas mixtures indicates that the concentrations derived from PTR-MS ion intensity measurements significantly underestimate the concentration of the aromatic compounds while overestimating the concentration of the oxygenated VOC’s.

1. Introduction
Mexico City with a population of nearly 20 million is one of largest metropolitan areas in the world. Situated in a high mountain valley with limited ventilation, Mexico City experiences significant air pollution problems associated with ozone and suspended particles. VOC’s play an important role in the light initiated reactions that lead to ozone and secondary aerosol formation. The Mexican government has funded a field measurement program to characterize the emission sources, the nature of the atmospheric transport and chemical transformations that lead to the atmospheric pollution within the Mexico City Metropolitan Area. In principal photochemical urban smog can be reduced by controlling emissions of VOC’s, NOx or both. Because it is not known whether the photochemical pollution is VOC or NOx limited canister sampling and PTR-MS programs have been funded to monitor the VOC’s as part of the field measurement program. The results obtained with a PTR-MS deployed as part of the February 2002 Mexico City Metropolitan Area field campaign are presented here.
2. Experimental

A standard version of the PTR-MS (Ionicon GmbH, Innsbruck, Austria) was used. Ambient air from a shared inlet line was sampled into the PTR-MS instrument at a flow rate of 15 sccm by use of a mass flow controller and flows through the drift tube at a pressure of 2 mbar and ambient temperature. \( \text{H}_3\text{O}^+ \) reagent ions created in an external hollow cathode ion source drift under the influence of an applied electric field through the reduced pressure ambient air sample where they undergo reactive collisions with those components having proton affinities greater than water, equation 1.

\[
\text{H}_3\text{O}^+ + \text{M} \xrightarrow{k} \text{MH}^+ + \text{H}_2\text{O} \tag{1}
\]

Under conditions where the reactive neutral, M, is present at trace levels the density of the product ion \( \text{MH}^+ \) is given by

\[
[\text{MH}^+] = [\text{H}_3\text{O}^+]_0[M]k_t \tag{2}
\]

where \([\text{H}_3\text{O}^+]_0\) is the density of the primary reagent ions, \(k\) is the reaction rate constant for the proton transfer reaction (eq. 1) and \(t\) is the reaction time. Collisional reaction rate constants calculated for both the \( \text{H}_3\text{O}^+ \) and its first hydrate \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) following the parameterized methods of Su and Chesnavich (Su and Chesnavich, 1982) were used and are listed in Table 1. The smaller oxygenated compounds react collisionally with both reagent ions whereas the aromatics only react with \( \text{H}_3\text{O}^+ \) (Warneke et al., 2001). The reactant ions and resulting ionic product ions are sampled through a small aperture where they are separated by a quadrupole mass filter and detected by a secondary electron multiplier operated in the pulse counting mode. Neutral number densities were calculated from the measured product ion intensities using the appropriate reaction rate constants and the measured drift times of \( \text{H}_3\text{O}^+ \) (1.06x10\(^{-4}\) sec) and \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) (1.11x10\(^{-4}\) sec) ions with the following equation.

\[
[M] = \frac{I_{\text{MH}^+}}{I_{\text{H}_3\text{O}^+}.k_c(\text{H}_3\text{O}^+)t_{\text{H}_3\text{O}^+} + I_{\text{H}_3\text{O}^+(\text{H}_2\text{O})}.k_c(\text{H}_3\text{O}^+(\text{H}_2\text{O}))t_{\text{H}_3\text{O}^+(\text{H}_2\text{O})}} \tag{3}
\]

Volumetric mixing ratios were determined by dividing the sample densities, from equation 3, by the drift gas total number density and are reported as ppbv. The quadrupole mass spectrometer was scanned from 20 to 200 amu at 0.5 seconds/amu repetitively and continuously over the sampling period. A switching valve was programmed to repeatedly admit ambient air directly into the instrument for twenty scans and then redirect the sampled ambient air through the catalytic scrubber, which provides a hydrocarbon free gas stream for ten scans to evaluate the instrumental background ion intensities. Active ions were identified by the characteristic intensity pattern created by the repeated sampling of the ambient and scrubbed air samples and the final reported concentrations are determined as the concentration difference between the ambient and scrubbed air samples.

**Table 1 PTR-MS ion assignments and calculated reaction rate constants**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Neutral precursor(s)</th>
<th>( k_c (\text{H}_3\text{O}^+) )</th>
<th>( k_c (\text{H}_3\text{O}^+(\text{H}_2\text{O})) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>Methanol</td>
<td>1.7x10(^{-9})</td>
<td>1.4x10(^{-9})</td>
</tr>
<tr>
<td>45</td>
<td>Acetaldehyde</td>
<td>2.2x10(^{-9})</td>
<td>1.8x10(^{-9})</td>
</tr>
<tr>
<td>59</td>
<td>Acetone + propanal</td>
<td>2.3x10(^{-9})</td>
<td>1.8x10(^{-9})</td>
</tr>
<tr>
<td>79</td>
<td>Benzene</td>
<td>1.9x10(^{-9})</td>
<td>-</td>
</tr>
<tr>
<td>93</td>
<td>Toluene</td>
<td>2.1x10(^{-9})</td>
<td>-</td>
</tr>
<tr>
<td>107</td>
<td>( \text{C}<em>8\text{H}</em>{10} + \text{C}_2\text{H}_6\text{O} )</td>
<td>2.2x10(^{-9})</td>
<td>-</td>
</tr>
<tr>
<td>121</td>
<td>( \text{C}<em>9\text{H}</em>{12} + \text{C}_8\text{H}_6\text{O} )</td>
<td>2.3x10(^{-9})</td>
<td>-</td>
</tr>
</tbody>
</table>
3. Results

Table 1 lists the ions monitored (excluding hydrates) and their most probable neutral precursor(s). Because of the complex nature of the urban air mass in Mexico City, characterization of the PTR-MS responses, which provides only mass information is limited to the seven compounds or classes of compounds listed in Table 1. Within this limited set of neutral precursors, methanol is the only single compound that can be positively identified. The ion at m/z 45 is probably representative of acetaldehyde unless high levels of ethanol are present in the ambient atmosphere. Ethanol reacts with O$_2^+$ via hydride abstraction to produce an ion at m/z 45. The isomeric carbonyls, acetone and propanal, can not be distinguished and the sum of these compounds is reflected by the intensity of m/z 59. The ion at m/z 79 represents protonated benzene but has contributions from the first hydrate of protonated acetic acid and from ion fragments of ethyl and propylbenzene. The ion at m/z 93 is primarily tolune, but may be influenced by ion fragments from ethyltoluene. Ethyltoluenes partially fragment upon proton transfer from CH$_5^+$ to form an ion at m/z 93 and a similar reaction may occur with H$_3$O$^+$. The C2-benzenes, which include the isomeric xylenes and ethylbenzene plus benaldehyde are detected at m/z 107. While the xylenes are the predominate contributor to this ion signal, benaldehyde and fragmentation products of higher order alkyl benzenes may represent significant interferences under certain conditions. Ethylbenzene fragments upon proton transfer and is only detected at about the 70% efficiency level. The ion at m/z 121 represents the sum of the C3-benzenes, which are the trimethylbenzenes, ethyltoluenes and propylbenzene plus the aromatic aldehyde and ketone C$_8$H$_8$O isomers. The ethyltoluenes and propylbenzene fragment upon proton transfer and are only partially accounted for.

The total PTR-MS response has been evaluated by summing the all of the product ion intensities. Not included in the sum are the proton hydrates H$_3$O$(H_2O)_n$ (n = 0 to 2), O$_2^+$ and NO$^+$. Using the total ion intensity and defining the reagent ion density by the intensity of H$_3$O$^+$ and a single reaction rate constant of 2x10$^{-9}$ mL/s provides an estimate of the PTR-MS total VOC concentration. The total concentration remained below 1 ppm for most of the sampling period validating the use of equation 2 to compute the sample concentrations. It was observed that the compounds listed in Table 1 represent approximately 50% of the total detectable VOC’s.

The PTR-MS instrument was operated at the regional air monitoring sites at La Merced, Xalostoc and Pedregal, which are located in the city center, industrial north and residential southern portions of Mexico City respectively. The measured VOC levels were similar at both La Merced and Pedregal while the levels were much higher at Xalostoc. However, the close proximity of an automotive painting facility at Xalostoc may be responsible for the elevated levels observed at this location. Methanol was found to be the most abundant compound with concentrations ranging between 10 and 100 ppbv while acetone (10-40 ppbv) and toluene (1-30 ppbv) concentrations were the next two most significant compounds observed. The temporal concentration profiles for all of the identified compounds were similar and highly correlated with changes in the CO$_2$ concentration indicating their source is predominately from vehicle emissions. Acetaldehyde concentrations observed at the Pedregal monitoring site were compared to the tunable diode laser formaldehyde measurements made over the same period, during which several significant photochemical events occurred. The correlation between these two data sets is very good and showed that significant amounts of acetaldehyde were being produced during the photochemical events observed during this time period. The most striking result of this comparison is that the acetaldehyde and formaldehyde concentrations were nearly equal. Except in urban areas where ethanol is a major automotive fuel component the acetaldehyde concentration is usually lower than the formaldehyde concentration. The high level of acetaldehyde relative to formaldehyde has raised concern about the accuracy of the PTR-MS acetaldehyde measurement.

Washington State University collected canister samples at the Pedregal monitoring site and this provided the opportunity to compare the PTR-MS measurements with the canister samples analyzed by gas chromatography (GC) using a flame ionization detector (FID) for those
compounds monitored by both techniques. The common compounds are primarily the aromatic hydrocarbons, benzene, toluene, the \( \text{C}_8 \text{H}_{10} \) isomers (xylene and ethylbenzene) and the \( \text{C}_9 \text{H}_{12} \) isomers (trimethylbenzene, ethyl toluenes and propylbenzene). Correlation plots for the PTR-MS and GC-FID measurements were made by reducing the PTR-MS measurements to 3-hour averages and by summing together the appropriate isomers of the WSU measurements. The slopes of the lines fitted to the plots of GC-FID versus PTR-MS concentrations and correlation coefficients of the fits are reported here for benzene \((m = 1.21, r^2 = 0.45)\), toluene \((m = 0.83, r^2 = 0.83)\), \( \text{C}_8 \text{H}_{10} \) \((m = 0.96, r^2 = 0.93)\) and \( \text{C}_9 \text{H}_{12} \) \((m = 0.90, r^2 = 0.83)\). The agreement between the two methods is very good with the differences lying within the +/- 20% range. Except for benzene the PTR-MS concentrations were slightly lower than those obtained with the GC-FID.

To validate the mixing ratios predicted by the PTR-MS, several post campaign calibration experiments were conducted. A calibrated standard containing methanol, acetaldehyde, acetone, benzene, toluene, \( \text{p-xylene and } 1,2,4\)-trimethylbenzene in compressed nitrogen was volumetrically diluted with background air and delivered to the inlet of the PTR-MS. A second series of experiments were performed using an in-house standard containing methanol, acetone, benzene and toluene prepared by volumetrically injecting the pure compounds into a sealed container. A single 1 mL aliquot of this standard was taken and injected into an exponential dilution volume that was connected to the inlet of the PTR-MS. The dilution gas was catalytically scrubbed background air. Experiments were done at normal humidity and by bubbling the dilution gas through water to examine the effect of humidity. Using the calibrated standard the concentrations derived from the ion intensity measurements for the oxygenated compounds agreed within +/- 20% level, methanol (+20%), acetaldehyde (-11%) and acetone (+20%) whereas the concentrations derived for the aromatic compounds were uniformly low by 40%. Using the exponential dilution technique the concentration delivered to the PTR-MS is defined by the relationship \( C_t = C_0 \exp(-t*F/V) \) where \( C_0 \) is the initial mixing ratio, \( t \) is the time after injection and \( F/V \) is the ratio of the volumetric flow rate of the dilution gas divided by the volume of the diluter. The concentrations predicted by the exponential diluter were in poor agreement with those computed from the PTR-MS ion intensity measurements for all of the substrates independent of the humidity level. The predicted PTR-MS responses were high for methanol (50%) and acetone (30%) while again being low for benzene (-30%) and toluene (-30%). While there may be considerable uncertainty in the concentrations calculated using the exponential diluter there appears to be a trend for the PTR-MS ion intensity derived concentrations to be low for the aromatic compounds. It was also observed in the exponential dilution experiments that the transmission correction factors may have a humidity dependence. These results indicate that the PTR-MS may require calibration.

4. References
Urban air measurement in Tokyo area using PTR-MS and comparison with GC-FID

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ABSTRACT

Ambient air at the suburb of Tokyo was measured by PTR-MS. Anthropogenic species show similar concentration change. Biogenic and oxygenated species show daily variation, but some of them could be influenced by interference masses. The comparison with PTR-MS and GC-FID results shows quite good correlation, but the absolute concentrations have some difference. The procedure of calculating the concentration is explained and possible error is discussed.

1. Introduction

Tokyo is one of the most polluted areas in the world (population is ca. 12 million in Tokyo Prefecture). Air quality issue, especially photochemical oxidants is focused on not only mid-city area but also on the semi-urban areas. The NO\textsubscript{x} emitted in urban area would survive to be transported to semi-urban areas and play a role to produce ozone under relatively high reactive hydrocarbons emitted from plants in suburban. To understand the photochemical reaction mechanism and obtain knowledge of key factors controlling air quality typical hydrocarbons were monitored in many cases. However the observations of more reactive hydrocarbons, reaction intermediate species, and oxygenated hydrocarbons are limited. PTR-MS enables the observation of such kind of reactive species and will make great help to understanding the reaction in urban area.

However very powerful tool to measure VOCs PTR-MS is, we need to be careful of quantification and quantification of VOCs. The measured species are determined only mass number, and there may be a interference species (and fragment peaks) at the same mass. The absolute concentration of VOCs can be deduced theoretically by PTR-MS. But there are something to be take account, for example, fragmentation, humidity dependence, etc. Therefore, if it possible, it is better to do crosscheck the PTR-MS data with the results by other more established method (for example, GC-FID).

2. Method

We are monitoring ambient air at the campus in Tokyo Metropolitan University, where is located about 30 km west of the center of Tokyo. It is suburban, residence area (but would be many traffic and human activity compared with other cities). Some selected species were monitored by PTR-MS (provided by IONICON). The zero air (generated by charcoal trap or heated Pt catalysis) was regularly injected to check zero level. PTR-MS was operated at the standard condition (2mbar and 590V at drift tube; corresponding to about 130 Td). At the same time, other atmospheric species (O\textsubscript{3}, CO, SO\textsubscript{2}, NO\textsubscript{x}) were measured by other instruments.

To compare the results with PTR-MS, some hydrocarbons (isoprene, benzene, toluene, C8-benxene, C9-benzene, terpenes) were also measured by GC-FID. The air was sampled at the same air inlet of PTR-MS using T connector, and concentrated by 3-stage pre concentrator (Entech7000). 500 ml air sampled at 150ccM was injected into GC-FID (HP6890). The column is HP-1 (length 60m, inner diameter 0.32mm, film thickness 1.0µm). Identification and concentration were determined using standard gas (Matheson, Enviro-MAT, mixture of 56 hydrocarbons at 1ppm).

3. Results and Discussion
The average daily concentration variations in August in 2002 at Tokyo metropolitan university are shown in Figure 1. The ambient air data was reduced by the zero air data. The concentration changes of the anthropogenically emitted species (benzene, toluene, C8-benzene, and C9-benzene) are quite similar. When plotting their correlation, they become very good straight lines, and this indicates their same origin, mostly from car exhaust. Their concentration change seems to have influenced by the condition of air (formation of inversion layer, transport from city center area) rather than the local traffic condition (rush hour in the morning and night). They are usually high at night because surface polluted air stagnate on the ground surface. At daytime, surface air is mixed easily with clean air at high altitude.

Since there are many trees in the university campus, isoprene and terpenes (they are emitted from plants) are also observed. Isoprene shows typical daily variation, high during daytime and low during night, since the mission of isoprene from plants is strongly dependent on light intensity and remove quickly (1-3 hour) from the atmosphere by the reaction with OH radical and ozone. But the isoprene (and other short lived species) measured by PTR-MS is not zero even at night and this would indicate the selected mass number is affected by interference signals. Oxidation products of isoprene (methyl vinyl ketone and methacrolein at mass 71) are also high during daytime, indicating quick oxidation of isoprene in the atmosphere. Short-lived species containing oxygen (formaldehyde and acetoaldehyde), they produced from oxidation of hydrocarbons, show daily cycle: high during daytime and low at night. But acetone and alcohol did not show clear daily variation.

Ambient air was measured by PTRMS and GC-FID at the same time in November, 2002. The common species measured by both instruments are isoprene (M69), benzene (M79), toluene (M93), C8-benzene (M107: xylenes, ethylbenzene, styrene), C9-benzene (M121: trimethylbenzenes, propylbenzenes), terpenes (M137: a-pinene, b-pinene, limonene, camphene). The observed results of benzene are shown in Figure 2. It can be seen that there is good agreement between the results of PTR-MS and GC-FID. The correlation plot of benzene measured by PTR-MS and GC-FID is shown in Figure 3. PTR-MS values are the average of 4 minutes corresponding to the sampling time for GC-FID measurement. The correlation is satisfactory. The intercept of the least square fitting line is near zero (through the origin). This indicates that the targeted mass has no interference. But the slope (absolute concentration) has some difference (0.82). The summary of the correlation plots for other species are listed in Table 1. The linearity of the correlation plot is also good for other species. But the slopes of PTRMS and GC-FID results are different for each species. The fitting line of isoprene has significant intercept and this indicate there is interference at mass 69. Checking the intercept of the correlation plot is a one method to check the interference.

Since the absolute concentrations are some difference between PTR-MS and GC-FID measurements, possible reasons of this difference will be discussed. Basically the targeted VOC concentration will be calculated by the equation (1).

\[ [\text{VOC}] = \frac{i[\text{VOC}^+]}{(k \cdot i[H_3O^+] \cdot t)} \]  

\( (1) \)

The signal of PTR-MS needs to be considered some factors to obtain true concentration. The possible factors need to be considered are listed below.

[A: transmission] The ion counts \( i[\text{VOC}^+] , i[H_3O^+] \) need to be corrected by the transmission factor of Q-mass for corresponding mass number. (This factor is already taken into account for the program provided IONICON.)

[B: parameters] The reaction rate constant \( k \) is different for each VOC. It is about \( 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) and this value is used as default (for the species that reaction rate constants are not available). If the true rate constant is \( 2.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \), the calculated result has 10 % difference. The reaction time \( t \) (average time of staying in the drift tube) is not easy to measure, but it can be deduced by calculation. I use the default value (105 µs).

[C: isotope] Most of VOCs makes its isotope peak, since carbon contain about 1.1% of C\(^{13}\). If the carbon number in the VOC increases, the existence of the isotope peak become not
negligible. For example, terpenes have 10 carbon atoms in a molecule, and they have about 10% of isotope peak (M137:M138 is about 9:1).

[D: fragmentation] Some species make fragmentation peaks at high E/N condition, especially terpenes. True concentration needs to be taken account for the fragment peak in addition to the main mass peak. For example, at our measurements setting, a-pinene has peak at mass 137 & 138 (main peak & its isotope) and mass 81 & 82 (fragment peak & its isotope). Their intensity is about 40% and 60%, respectively. If only mass 137 is taken account, the results will be only about 40% of the true value.

[E: water cluster] If the measuring air is very humid and E/N setting is low, the targeted VOC could make water cluster (VOC•H₂O). In this case, the VOC will be calculated lower than the true concentration. The mass of the cluster ion needs to be monitored (+18).

[F: reaction ion cluster] The reaction ion H₃O⁺ makes clusters H₃O⁺(H₂O)ₙ (n=1,2,...) in the drift tube, especially at low E/N condition. Some VOC can react with H₃O⁺(H₂O)ₙ and the reaction rate constant is almost same as H₂O⁺. In this case, sum of H₂O⁺ and H₂O⁺(H₂O)ₙ should be the reaction ion. If VOC does not react with H₂O⁺(H₂O)ₙ, only H₂O⁺ should be the reaction ion. But the real situation is a little bit complicate. Some of the cluster dissociated before the detection chamber, and the detected ion could not give the true distribution of clusters in the drift tube. Warneke et al. (2001) discussed about this issue.

[G: instrument setting] The sensitivity of SEM will decrease after some use. If SEM voltage setting is not proper (lower voltage), the calculated concentration become lower. Tuning of the mass peak (mass position and mass width) is also necessary.

[H: GC-FID] The difference between GC-FID and PTR-MS will be a part of the error of GC-FID measurements. There will be uncertainty of standard gas using for GC-FID measurement. Also there might be uncounted species in GC-FID which makes a peak at the same mass number. The comparison results of the our measurements is taken account above [A,B,C,D, and G]. Therefore the difference would be caused by other factors I did not considered. Because of the difficulty to know the true distribution of H₂O⁺(H₂O)ₙ in the drift tube, the easy way to ensure the PTR-MS result is measuring a few samples by GC-FID at the same time and comparing to it. (if [H] is not the case.)

Acknowledgement
Authors thank to Dr A. Jordan (IONICON) for kindly replies to many questions. We also thanks to Dr A. Tani at Tokai University for helping practical operation of PTR-MS. On of the author thanks to T. Kaneko for helping GC-FID measurements. This work is supporred by CREST of Japan Science and Technology corporation.

Reference
**Figure 1** Dairy average variation of VOCs in August at Tokyo Metropolitan University

**Table 1** Slope and intercept of MTR-MS and GC-FID correlation plots

<table>
<thead>
<tr>
<th>Substance</th>
<th>Slope (a)</th>
<th>Intercept (b)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene</td>
<td>1.40</td>
<td>138</td>
<td>0.72</td>
</tr>
<tr>
<td>benzene</td>
<td>0.82</td>
<td>26</td>
<td>0.90</td>
</tr>
<tr>
<td>toluene</td>
<td>0.61</td>
<td>183</td>
<td>0.95</td>
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<tr>
<td>C8-benzene</td>
<td>0.71</td>
<td>1</td>
<td>0.86</td>
</tr>
<tr>
<td>C9-benzene</td>
<td>0.98</td>
<td>-93</td>
<td>0.92</td>
</tr>
<tr>
<td>terpenes</td>
<td>0.96</td>
<td>33</td>
<td>0.84</td>
</tr>
</tbody>
</table>

**Figure 2** Comparison with benzene concentration measured by PTR-MS and GC-FID

**Figure 3** Correlation plot of benzene measured by PTR-MS and GC-FID
Applications of PTR-MS at JRC-Ispra in laboratory studies related to atmospheric chemistry

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ABSTRACT
A PTR-MS instrument, built by IONICON in Innsbruck (A), has been applied at the JRC in Ispra in studies related to atmospheric chemistry, with a focus on biogenic emissions of hydrocarbons and their subsequent chemical conversion in the atmosphere. PTR-MS was found to be a useful tool in kinetic studies of biological as well as chemical systems due to its high time resolution and sensitivity.

1. Introduction, Results and Discussion
The uptake of CO² and its subsequent incorporation in isoprene or monoterpene molecules emitted from vegetation was studied by exposing oak and pine species to isotopically labelled carbon dioxide (¹³CO²) in an enclosure where the plant was irradiated with artificial sunlight under controlled temperature and humidity conditions. The increasing ¹³C/labelling during exposure to ¹³CO² as well as the loss of ¹³C after return to normal ¹²CO² exposure could be followed by the PTR-MS instrument. In the case of isoprene it was found that more than 90% of the carbon atoms in the emitted hydrocarbon were ¹³C-isotopes after 20 minutes of exposure to ¹³CO².

In other studies the influence of light, temperature and water stress as well as rewatering on emissions from selected tree species was investigated. Independent checks of type and amounts of VOC emissions were made by GC-FID, GC-MS and HPLC (for more details about the experiments and the results, see reference 1).

The same PTR-MS instrument was applied in laboratory experiments in combination with FT-IR (Fourier Transformed Infrared Spectroscopy) to investigate the formation of acetone and other oxidation products formed by the degradation of monoterpenes (α- and β-pinene) initiated by the reaction with OH radicals.
The experiments were performed in a 480 l chamber equipped with a multipass mirror system for IR-measurements. The on-line PTR-MS measurements allowed to follow the kinetics of the reaction and the analysis of the data showed that acetone was formed both as a primary product and as a secondary product, i.e. via the degradation of stable, primary products.

Figure 1 shows the variation of reactant and products during a typical experiment (for more details about the experiments and the results, see reference 2).

![Figure 1](image.png)

Figure 1. Measured variations of products and reactants as a function of time from the reaction between α-pinene and the OH radical during a typical experiment. The acetone concentration is corrected for the release of acetone from the chamber walls (Figure taken from Ref. 2).

Presently, PTR-MS is being used in similar laboratory studies focused on the identification and quantification of the short-lived, reactive intermediates of VOC oxidation that can not easily be analysed with other, more traditional techniques that require either higher concentrations of analytes (e.g. FTIR) or are based on non in-situ analysis that require sample collection and storage (e.g. LC-MS).

Many of the gaseous oxidation products are semi-volatile in nature and in order to make reliable, time-resolved measurements the adsorptive losses and memory effects of these compounds in the sampling device have to be minimised. This was done by heating the inlet and drift tube of the PTR-MS instrument to $80^\circ$ C.
In a drift tube reactor ions are accelerated by an electric field relative to surrounding buffer gas (ambient air). This leads to energetic collisions between the ions and the buffer gas. By optimising the E/N (that is proportional to the square root of the collisional energy) it is possible to minimise clustering and thus the formation of hydrated molecular and reactant ions that complicate the analysis of mass spectra. However care has to be taken in order to minimise the fragmentation of protonated analytes that can lead to even more complicated and less predictable mass spectra than the hydration alone. This is especially important for high-molecular-weight aldehydes since these compounds fragment already at thermal energies.

The influence of the drift tube voltage on the fragmentation and hydration of the protonated analytes was investigated for a series of volatile organic compounds. The results of this work were used to optimise the conditions used during the laboratory experiments (see Fig. 2).

![Graph showing the contribution of the molecular ion (MH⁺), fragments, and the hydrate (MH⁺H₂O) to the total cyclobutanecarboxaldehyde signal as a function of E/N. Cyclobutanecarboxaldehyde was added in dry air.](image)

Figure 2. Contribution of the molecular ion (MH⁺), fragments and the hydrate (MH⁺H₂O) to the total cyclobutanecarboxaldehyde signal as a function of E/N. Cyclobutanecarboxaldehyde was added in dry air.

2. References


Deploying a PTR-MS onboard passenger aircraft (Project CARIBIC) for on-line monitoring of volatile organic compounds in the UTLS

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ABSTRACT
A Proton-Transfer-Reaction Mass Spectrometer system is modified for automated continuous on-line measurement of volatile organic compounds (VOC) onboard a passenger aircraft. Within CARIBIC (Civil Aircraft for Regular Investigation of the atmosphere Based on an Instrument Container) altogether ~60 trace gases and ~20 aerosol parameters are measured at 8-12 km altitude using an Airbus 340-600 operated by Lufthansa as of September 2003 on a monthly basis. Compounds of interest include acetone, acetaldehyde, methanol, toluene, benzene and acetonitrile. The data will give information on the budgets of these trace gases in the upper troposphere and lower stratosphere (UTLS), on transport processes and on chemical processing such as the local oxidation capacity. Up to now only a limited number of measurements of VOCs are available in the UTLS exclusively gathered during short-term research aircraft campaigns. CARIBIC allows for long-term observations and thus yields a complementary dataset that is particularly valuable for comparisons to atmospheric model results and for inference of seasonal and inter-annual variations.

1. The CARIBIC Project
The concept of CARIBIC is to use regularly operating passenger aircraft for measurements of atmospheric characteristics in the UTLS. This region belongs to the least well-known areas of the atmosphere, mainly because of its extreme dynamical complexity and the scarcity of accurate data. In comparison to research aircraft used during short-term campaigns this concept is a relative cost-effective alternative for collection of detailed information about the UTLS. Within CARIBIC a reinforced airfreight container equipped with different instruments is installed into the cargo bay of a passenger aircraft. After a built-up phase started 1993, first measurement flights were conducted using a Boeing 767 by LTU International Airlines. Up to May 2002 more than 80 successful flights took place. In this first phase on-line measuring devices for the following trace species have been operated: carbon monoxide (Max Planck Institute for chemistry (MPIC), Mainz, Germany), ozone (Institute of Meteorology and Climate Research (IMK), Forschungszentrum Karlsruhe (FZK), Germany), aerosol concentration (Institute for Tropospheric Research (IfT), Leipzig, Germany) and nitrogen oxides (NO, NO₂) (German Aerospace Center (DLR), Oberpfaffenhofen, Germany). Furthermore, the elemental aerosol composition was measured (University of Lund, Sweden) and canister samples were taken,
which were subsequently analysed in the laboratory for ~15 hydrocarbons (mainly alkanes and alkenes), the isotopic composition of CO and CO\(_2\) (MPIC), and halocarbons (University of East Anglia (UEA), UK). Detailed meteorological support such as back-trajectory trajectory analyses was provided by the Royal Netherlands Meteorological Institute (KNMI, de Bilt, Netherlands).

The first phase was terminated with the sale of the Boeing 767 by LTU. An overview on the first phase of the project and first results are given by Brenninkmeijer et al. [1999] and Zahn et al. [2000, 2002]. For a second phase of CARIBIC a new airline was found with Lufthansa AG. Currently a brand-new Airbus 340-600 is re-built for starting new measurements as of September 2003. The new cooperation gave us the chance to install an even bigger container (total weight: ~1300 kg) and to add new instruments. Additional measurements will include, inter alia, CO\(_2\) (Centre de la Recherche Scientific (CNRS), Gif-Sur-Yvette, France), BrO, CH\(_2\)O, NO\(_2\), SO\(_2\) (University Heidelberg, Germany), H\(_2\)O (for water vapour and cloud water, IMK), Hg (GKSS research center, Geesthacht, Germany) and VOCs (IMK). The VOCs will be measured using the PTR-MS. The modification on this instrument will be described next.

2. Modifications on the PTR-MS system
The PTR-MS system, developed by the University of Innsbruck [Hansel et al., 1995; Lindinger et al., 1998], was bought in its commercially available design. Technical changes are necessary for using the PTR-MS on passenger aircraft. The aircraft power supply serves 28 VDC. Also power consumption, instrument seize and weight have to be optimized to a minimum. Thus, the PTR-MS power supply has to be changed from 220 VAC onto 28 VDC. AC/DC converters for the high voltage parts and DC/DC converters are installed for that reason. The DC/DC converters are also equipped with effective electronic filters to inhibit interferences of the instrument power consumption with the aircraft power and vice versa. The PTR-MS is set on shock mounts to suppress aircraft hits on the turbo molecular pumps and to reduce influences on the radio frequency. The whole system is installed into an extremely stable rack specified for the use on airplanes. This rack will be mounted into the new CARIBIC container similar as in the old container shown in figure 1.

Further modification on the PTR-MS system include a unit for online calibration during flight and a zero air filter (Pt-catalyst) for determining the background signal of the mass spectrum.

The time table is set that the PTR-MS system is set up in its configuration for the use on the airplane in January 2003. Laboratory tests will be performed until spring 2003. In summer the final version will be put into the container and the installation of the container on the Airbus 340 will be performed in September 2003. After installation the first automated measurement flight should start. Measurements are planned to continue for at least 10 years.
3. Scientific interest

The PTR-MS provides a powerful tool for measuring oxygenated organic compounds and nitriles in the atmosphere [e.g. Hansel et al. 1995]. Oxygenated hydrocarbon species can easily be photolyzed throughout the troposphere. Therefore they are precursors of $\text{HO}_x$ ($\text{HO}_2 + \text{HO}$) free radicals and may influence the ozone formation potential and the oxidizing capacity of the atmosphere [Singh et al., 1995; 2001]. They can also contribute to the organic component of aerosols [Singh et al., 2001] and they are linked to the chemistry of reactive nitrogens. Acetone can also form peroxyacetyl nitrate (PAN) in the upper troposphere and sequester reactive nitrogen [Wennberg et al., 1998]. Otherwise some volatile organic compounds can be used as tracers for transport processes. Acetonitrile can be regarded as tracer for biomass burning [Bange and Williams, 2000], whereas toluene and benzene are indicators for industrial emissions.

Exchange between the troposphere and stratosphere, long range transport and convective transports will be particularly investigated during CARIBIC. This project will give the chance to investigate processes on global and seasonal time scales overcoming the problems of spot measurements during short-term campaigns which only provide an instantaneous state of the atmosphere. The free atmosphere will be monitored over a time interval of about 10 years, allowing a comparison of the present and future composition of the free atmosphere. A
distinction between natural and anthropogenic sources of chemicals is possible. Data are achieved for validation of models and satellite data. Budgets of trace gas in the UTLS region may be estimated. The trace gases can be used as tracers for troposphere-stratosphere exchange. Emissions of the US, Europe, Africa, and Asia can be estimated. The influence on the transport of the Indian and Mexican monsoon can be investigated. Biomass burning i.e. the influence of deforestation in Africa, South America and Asia can be examined. The influence of the air traffic is also of interest.

References:
PTR-MS measurements of acetonitrile, acetone and methanol: new implications and applications in the field of atmospheric chemistry

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ABSTRACT
The PTR-MS technique has been used in many field and laboratory experiments to measure concentrations of acetonitrile, acetone and methanol. Since 1999 several studies and campaigns have been performed by the Max Planck Institute of Chemistry; some important results from these experiments are presented here. All three compounds are emitted during biomass burning in significant concentrations. For acetone and methanol we have found strong evidence that emission factors measured in experimental fires are not representative for natural conditions. Due to secondary production of acetone and methanol in plumes the actual production from biomass burning is likely enhanced by a factor of 2-5 compared to previous assumptions. If this proves to be correct the contribution of biomass burning emissions of acetone and methanol to the global budgets is currently severely underestimated.

1. Acetonitrile
Acetonitrile has been proposed as a tracer for biomass burning emissions (Lobert et al., 1990). However, great uncertainties still exist about its atmospheric lifetime and sinks. There has been much speculation about acetonitrile sources other than biomass burning (Hamm and Warneck, 1990) but as yet no evidence for any major additional sources has been found. The frequency distribution of acetonitrile, as measured in the troposphere (0-13 km) over the Eastern Mediterranean, is in accordance with a lifetime of 1.3 years. Besides reaction with hydroxyl radicals, dry deposition of acetonitrile has been observed over land and sea. Preliminary results from a recent cruise in the tropical Atlantic suggest that oceanic uptake of acetonitrile does not play a significant role over large regions of the ocean.

Using the PTR-MS technique fast measurements of acetonitrile can be used to assess the biomass burning fraction of other compounds (Holzinger et al., 2003). This fraction can be calculated by multiplying compound-specific production factors relative to acetonitrile by the enhancement of acetonitrile mixing ratios above background for each point in the dataset. Figure 1 shows acetonitrile data from the Mediterranean Intensive Oxidants Study (MINOS) in August 2001, together with a statistical evaluation. The average was significantly lower than the median mixing ratio (0.5 percentile in Figure 1) for the lowest two altitude levels. From trajectory analysis (Traub et al., 2003) it can be demonstrated that these air masses were not mixed with very clean background air, so we are able to conclude that the observed acetonitrile variability in the lowest 4 km of the troposphere is high due to a strong influence from both biomass burning sources and uptake into the sea. Interestingly variability also increases at altitudes above 11 km. Based on the trajectory analysis, this effect is attributed to fresh pollution convected by the monsoon from south Asia where, biofuel use is common.
Figure 1. Acetonitrile volume mixing ratios measured over the Eastern Mediterranean in August 2001 (MINOS).

2. Methanol

The tropospheric budget of methanol is extremely uncertain. The estimated global source (~120 Tg yr\(^{-1}\)) is not at all well balanced by the known sinks, which are in the order of 45 Tg yr\(^{-1}\) (Singh et al., 2000). During the MINOS campaign methanol was better correlated with acetonitrile ($R^2=0.41$) than carbon monoxide ($R^2=0.33$) – a molecule which is also used as an indicator for biomass burning.

The importance of biomass burning emissions to the budget of methanol can also be seen in data obtained from two campaigns at a site the middle of a vast woodland savanna near the city of Calabozo, Venezuela (8°52’N, 67°10’W). Measurements in both seasons (wet season: Sept/Oct 1999; dry season: Mar/Apr 2000) yielded similar levels of methanol during daytime when the nocturnal layer was broken up; the observed mixing ratios are typical for boundary layer conditions (Figure 2). Taking into account the fact that the oxidation capacity and the boundary layer height are lower in the wet season (lower solar radiation and wind speeds), the source of methanol in the dry season must exceed the biogenic source during the wet season. Since vegetation productivity is very low at this time of the year, we conclude that biomass burning is by far the dominant source of methanol during the dry season. Assuming that about 100 of the 250 pmol/mol of acetonitrile measured during daytime are background, the ratio methanol/(acetonitrile-acetonitrile background) is in reasonable agreement with the value (24.9) obtained from several biomass burning plumes sampled over the Eastern Mediterranean during the MINOS campaign. Provided that this ratio is representative, it follows that biomass burning emission factors for methanol are higher by a factor of 2-3 than the values which are reviewed by Andreae and Merlet (2001) and are currently used in most models.
3. Acetone

Acetone is directly emitted from biomass burning. We have conducted several laboratory studies which have yielded emission factors in good agreement with values reviewed by Andreae and Merlet (2001). Recently Jost et al. (2002) have observed secondary production of acetone in a biomass burning plume over Namibia. Their findings are strongly supported by our results, obtained from both biomass burning plumes over the Eastern Mediterranean, and measurements of acetone in the Venezuelan savanna during the dry season. In natural plumes acetone emission relative to CO was found to be 0.025 mol/mol, on average, which is more than 5 times higher than the values commonly used.

Figure 3 shows the preliminary results from acetone measurements during a research cruise across the tropical Atlantic aboard the German research vessel FS Meteor. One PTR-MS instrument was connected to a purging system, in order to measure oxygenated compounds in surface seawater. Ambient air mixing ratios were monitored with a second PTR-MS. To compare water with air concentrations the seawater concentrations are expressed here as equilibrium gas-phase mixing ratios which, were obtained by multiplying the water concentrations by the Henry’s law constant. Two distinct periods were observed where acetone was emitted from the ocean into the atmosphere. The first (Oct. 19-21 2002) coincided with a plume of fresh water from the Amazon, which was detected by remote sensing and reduced salinity at the surface. During the second period (Nov. 5-8 2002) we were in coastal waters near Guinea-Bissau. Assessment of the strength and relevance of these fluxes is currently in progress.
Figure 3. Acetone concentrations in surface seawater, expressed as equilibrium gas-phase mixing ratios, together with acetone mixing ratios in the marine boundary layer.

4. References
Traub, M., H. Fischer, et al. (2003). "Chemical characteristics assigned to trajectory clusters during the MINOS campaign." submitted to ACPD.
On-line analysis of VOC emissions from Sitka spruce (*Picea sitchensis*)

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ABSTRACT

This paper presents the application of PTR-MS to the measurement of the volatile organic compounds (VOCs) isoprene (2-methyl-1,3-butadiene) and acetaldehyde (ethanal), emitted from the coniferous tree species Sitka spruce (*Picea sitchensis*). Emissions were monitored on-line using laboratory based specimens and emission rates determined in response to differing light and temperature regimes using dynamic enclosure techniques. In addition, PTR-MS was used to monitor the rate and extent of incorporation of $^{13}$C into emitted isoprene following exposure to $^{13}$CO$_2$ at ambient concentrations. Emissions of isoprene showed typical light and temperature dependency, and a ‘basal’ emission rate at standard conditions of $\sim 25$ µg g$^{-1}$ dw (dry weight) h$^{-1}$. However, the emission capacity of this species was found to shift considerably over a 5 day period following the implementation of different growing conditions. Following each daily photo-period (14 h), a transient post-illumination burst of acetaldehyde was observed which coincided with a depression in isoprene emissions. Further experimentation showed that lengthy acetaldehyde bursts (i.e. elevated emissions) could not be maintained or induced by prolonged leaf flecking. Labelling of isoprene with $^{13}$C occurred almost immediately after exposure to $^{13}$CO$_2$, and within 5 minutes all mass-possibilities (69 – 74; fully unlabelled – fully labelled) were detectable. A steady state, dominated by fully labelled isoprene ($\sim 42\%$) was reached within $\sim 2$ h, at which point 80% of all isoprene carbon atoms were $^{13}$C labelled.

1. Introduction

Isoprene is a C$_5$ the volatile organic compounds (VOC) emitted in significant quantities from many plant species, particularly woody trees (Fehsenfeld *et al.* 1992). Emissions are both light and temperature dependent. The physiological function of isoprene remains unclear, although recent evidence points towards a role in thermal protection during transient high temperature episodes (Sharkey *et al.* 2001). Less disputed however is the role played by isoprene in the lower troposphere where its high reactivity towards the OH radical can bring about tropospheric ozone production (Chameides *et al.* 1988). Acetaldehyde is a C$_2$ hydrocarbon whose emissions from vegetation have been associated with anoxia or hypoxia, particularly during root flooding (Kreuzwieser *et al.* 1999). In addition, emissions have also been linked with wounding, senescence and leaf stress (Fall *et al.* 1999, Kimmerer and Kozlowski 1982).
More recently, it has been hypothesised that ‘bursts’ in acetaldehyde emission rates during light-to-dark transitions result from a pyruvate overflow mechanism (Karl et al. 2002a). Like isoprene, acetaldehyde can also play a significant role in tropospheric oxidative chemistry.

In this paper, PTR-MS is used to monitor the emission rate of the VOCs isoprene and acetaldehyde from Sitka spruce (*Picea sitchensis*). Measurements were made in response to changing light and temperature regimes using whole branch and stem cuvette enclosure systems. A further exercise investigated VOC emissions over a 10 day period following the introduction of a specimen to a warmer, brighter (14 h photo-period) environment. In addition, the rate and extent of incorporation of $^{13}$C from exogenously fed $^{13}$CO$_2$ into isoprene was monitored by measuring protonated masses 69 (fully unlabelled) through to mass 74 (fully labelled).

2. Results and discussion

Isoprene emissions showed typical light and temperature dependency (Fig. 1) and using the categories defined by Guenther et al. (1994), Sitka spruce was classified as a ‘moderate’ isoprene emitter under standard conditions. The basal isoprene emission rate was $\sim 25$ µg g$^{-1}$ dw h$^{-1}$ at 30°C and 1000 µmol m$^{-2}$ s$^{-1}$ PAR (photosynthetically active radiation). Maximum emission rates of over 40 µg g$^{-1}$ dw h$^{-1}$ were achieved at $\sim 300$ µmol m$^{-2}$ s$^{-1}$ PAR and 40°C needle temperature.

![Figure 1](image1.png)

**Figure 1.** Sitka spruce isoprene emissions as (a) a function of PAR at a constant needle temperature of 30°C and (b) a function of leaf temperature at a constant PAR exposure of 300 µmol m$^{-2}$ s$^{-1}$ (saturation).

The ‘basal’ isoprene emission rate of an outdoors acclimated specimen was found to increase almost 3-fold over a 5 day period following introduction to a warm (22 – 32°C), illuminated (14 h photo-period) environment, consistent with an increase in isoprene synthase activity (Lehning et al. 1999). Immediately after each photo-period (light-to-dark transition), a
burst of acetaldehyde was observed, whose magnitude was typically double that of the maximum isoprene emission rate for that day (Fig. 2).

![Graph showing Isoprene and Acetaldehyde emission rates](image)

**Figure 2.** Sitka spruce isoprene and acetaldehyde emission rates (µg g\(^{-1}\) dw h\(^{-1}\)) following a light-to-dark (300 - 0 µmol m\(^{-2}\) s\(^{-1}\) PAR) transition.

However, further experimentation showed that bursts of this magnitude could not be maintained during prolonged leaf-flecking. In addition, a simultaneous post-illumination ‘depression’ in isoprene emission rate was also observed. \(^{13}\)C labelling of isoprene occurred almost immediately following exposure to \(^{13}\)CO\(_2\) and within 5 minutes all protonated isotopes (69 – 74) were detectable. The abundance of unlabelled isoprene showed rapid decline during this period while the abundance of isotopes of mass 70 and 71 initially increased then decreased (Fig. 3a). The abundance of the other isotopes (72 – 74) increased during this period and a steady state was reached within ~ 2 h, with the emission spectrum dominated by fully labelled isoprene (Fig. 3b). In total, ~80% of isoprene carbon was labelled at steady-state. The presence of unlabelled isoprene carbon after 2 h exposure to \(^{13}\)CO\(_2\) suggests more than one carbon source for the precursors of isoprene production, consistent with the findings of Karl *et al.* (2002b).
Figure 3. (a) Incorporation of $^{13}$C from $^{13}$CO$_2$ into emitted isoprene; 69 = fully unlabelled protonated isoprene, 74 = fully labelled protonated isoprene. Emission rates given as µg g$^{-1}$ dw h$^{-1}$. (b) Steady-state abundances of isoprene isotopes emitted from Sitka spruce; 300 µmol m$^{-2}$ s$^{-1}$ PAR, 25°C leaf temperature.

3. Acknowledgements

The authors would like to express thanks to Sue Owen, Antonia James and Akira Tani, and to the U.K. Natural Environment Research Council (grant number GR3/12750).

4. References

Terpene hydrocarbons are ubiquitous compounds in the atmosphere. Frits Went, in 1960 suggested that the volatile organic emissions from plants especially the monoterpenes were responsible for the formation of the atmosphere’s ‘blue haze’. Recent surveys of plant emissions using the PTR-MS have shown that many species emit sesquiterpenes (Ssqt’s) independent of emitting monoterpenes or isoprene. A more probable immediate source of the organic micro-aerosols responsible for scattering the blue end of the spectrum, i.e. ‘blue haze’ are the more rapid reactions of the sesquiterpenes rather than monoterpenes with ozone resulting in particles. Ambient concentrations are site dependent, but are typically very low from a few to 100 pptCv, except for isoprene which has summer mid-day median levels of 3 to 6 ppbCv. The sesquiterpenes are very difficult to measure in the atmosphere by conventional means but copaene, cubebene, bourbonene and beta-caryophyllene are common foliage emissions. Is the difficulty in measuring low levels of sesquiterpenes in the atmosphere due to 1. Ssqt’s not emitted in sufficient amounts: dilution too great; 2. Ssqt’s react so quickly with ozone that atmospheric level is ~ zero and 3. Processing steps of capture and storage of Ssqt’s for subsequent analyses result in losses? Measurements of isoprene, monoterpenes and sesquiterpenes over plant foliages with a Proton Transfer Reaction - Mass Spectrometer were compared with captive samples of the air from the same plant foliages collected and stored in Summa canisters. None of the biogenic organic emissions stored in the Summa canisters showed any significant losses due to wall effects. Neither did we observe that any of the processing steps were responsible for losses or internal molecular rearrangements. The reason for the stability and 100% recovery of these C5 to C15 olefinic compounds at room temperature is believed to be due to the water layer formed on the walls of the canister under pressure at 30 psig. Ozone added to the test systems was observed to have an immediate effect on the sesquiterpenes at ambient levels. This suggests that the very rapid rates of reaction of Ssqt’s with ozone are an important and immediate removal mechanism of ambient Ssqt to very low concentrations. Results from reaction with ozone added to the samples, recoveries with decreasing pressures in the canisters and Nafion dryers in line are discussed.
Eddy Covariance Measurements of Volatile Organic Compound Fluxes Using Proton-Transfer-Reaction Mass Spectrometry

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Interest in reliable quantification of organic trace compounds released from terrestrial ecosystems stems from their impact on oxidants levels such as ozone (O\textsubscript{3}) and hydroxyl radicals (HO) and on secondary organic aerosol formation (Atkinson R., 1994). Oxygenated species can also influence the HO\textsubscript{x} budget in the upper troposphere (e.g. acetone) and affect CCN/IN (cloud condensation nuclei / ice nuclei) properties of tropospheric aerosols. Together with carbon dioxide, volatile organic compounds (VOCs) impact the atmospheric radiative balance, temperature and precipitation patterns (Granier et al., 1998). Emissions of VOCs are therefore important input parameters for atmospheric chemistry models. Regional air quality decisions, for example, rely heavily on correct emission estimates. In order to quantitatively understand tropospheric chemistry it is a necessary prerequisite to have reliable data on emission estimates and the processes controlling the exchange of reactive carbon. In the past couple of years we have explored the use of Proton-Transfer-Reaction Mass Spectrometry for eddy covariance flux measurements. This presentation will summarize the outcome from several flux studies (Biosphere II experiment, 2000, Niwot Ridge, 2001, Prophet 2001/2002, ), assess our current understanding of oxygenated compound fluxes and address future needs in order to improve VOC emission modeling.
Calibration and Application of PTR-MS for Biogenic VOC Measurements in a Deciduous Forest

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ABSTRACT

A PTR-MS system was tested and applied for a range of biogenic VOC's. The calculated trace gas concentrations of the PTR-MS agreed well with a diffusion calibration system if an up-to-date transmission function was included. The PTR-MS system was used for VOC measurements in a central European deciduous forest within the framework of the ECHO project. A considerable sensitivity drop of the PTR-MS during the field campaign was assigned to a shift in the detector response and could be corrected according to repeated cylinder standard measurements. The resulting time series for isoprene showed good agreement with parallel GC-FID measurements. The PTR-MS technique allowed fast measurements of four-level concentration profiles of various VOC species throughout the forest canopy at a time resolution of 20 minutes.

1. Introduction

Vegetation plays a major role within the biosphere-atmosphere-exchange of several volatile organic compounds (VOC). But there is still a lack of knowledge concerning the amount of reactive trace gases being emitted or deposited by forests and other ecosystems as well as the chemical processing of these compounds within the vegetation canopy. The quantification of biogenic VOC exchange on the ecosystem scale is still an analytical challenge. Fast and sensitive systems are needed for simultaneous measurements of several substances at a high temporal resolution. The PTR-MS (Proton Transfer Reaction Mass Spectrometry) has the potential to fulfil these requirements. However, there are still uncertainties about the stability and representativeness of PTR-MS signals, the accuracy of calculated concentrations and the necessity for calibrations. In the present text, we report about calibration and field application of a PTR-MS system for biogenic VOC measurements within the framework of the ECHO project (Emission and Chemical Transformation of Biogenic Volatile Organic Compounds, see http://www.fz-juelich.de/icg/icg-ii/ECHO/echo.ger.html). The field campaign was performed in a mixed deciduous forest stand at the terrain of the research centre Jülich (Germany) in summer 2002.

2. Measurement Setup

The applied instrument was a commercially available PTR-MS system (IONICON, Innsbruck Austria, 2000), which was operated at a drift tube pressure of 2.0 mbar. All inlet tubing were PFA with some fittings of stainless steel. The original inlet flow controller had been replaced by a pressure controller that maintained an inlet sample flow of about 150 ml/min. For determination of instrumental offsets, the sample flow was periodically directed through a catalytic converter filled with Platinum wool and heated to 450°C.

During the ECHO field campaign in June/July 2002, the PTR-MS was operated at the base of a 36 m high tower in the forest of the Jülich Research Centre, side-by-side to an online gas chromatography system with flame ionisation detector (GC-FID). Air was sampled through equally long tubes (50m) from four inlets on the tower at 9, 18, 27 and 36 m above ground. The height of
the forest canopy was about 30 m. The PFA sampling tubes were heated and flushed continuously at a rate of 3.5 l/min. Both gas analysing systems were switched alternatively to the four sample lines by PTFE solenoid valves. The measurement sequence of the PTR-MS was controlled by a script language program of the quadrupol unit. It switched between the profile levels every 5 or 10 min. and initiated offset measurements every one or two hours. Since up to 20 different masses were usually detected, the effective integration time per mass and profile level was less than about 30 s within one hour. The on-line GC-FID had a time resolution of ~30 min. VOCs were accumulated on solid adsorbents for 5 min. and then analysed within 25 min.

3. Concentration Calculation and Calibration Procedures

Trace gas concentrations for the PTR-MS measurements can be calculated from the ion concentration ratio of the protonated trace gas molecule and the educt ion (Lindinger et al., 1998):

\[
[R] = \frac{1}{k \cdot t} \cdot \frac{[RH^+]}{[H_3O^+]} 
\]

(1)

The reaction time \(t\) is 105 \(\mu\)s for the applied instrument, and the reaction constant \(k\) was set to the respective calculated thermal rate constant acc. to Lindinger et al. (1998). The used \(k\)-values for some VOC species are listed in Table 1. For calculating the correct ion concentration ratio in the drift tube, the respective count rates have to be corrected for the mass-dependent transmission of the detector. According to the manufacturer, the transmission function can be determined by adding a short excess concentrations of selected VOC's to the sample air stream, so that all the \(H_3O^+\)-ions are used up producing the respective VOC ions, and comparing both ion count rates. However, this procedure was found to give results with considerable scatter not suitable for obtaining an accurate continuous transmission curve. We therefore prepared air samples with adjusted VOC concentrations in Tedlar bags that provided a constant sampling concentration over several minutes and reduced the \([H_3O^+]\) signal by only 30-70%. The results of these measurements differed from the original manufacturers transmission curve at mass 19 by more than 30%.

The calculated concentrations of the PTR-MS measurements were compared to a VOC diffusion source calibration system in the laboratory at the Research Centre Jülich in Mai 2002 (very similar to the one described by Komenda et al., 2001). Table 1 lists some of the provided VOC species with the gravimetrically determined calibration concentration and the respective PTR-MS results. A fragmentation correction was made only for isoprene, for which a stable m41 fragment fraction of 15% had been observed, and for the monoterpenes, for which the main fragment mass m81 was added to the protonated molecule mass m137. The PTR-MS measurements generally tend to underestimate the calibration concentrations. However, the deviation is less than 10% for half of the species and equal or less than 25% for the rest.

Table 1: Results of the laboratory calibration of the PTR-MS with a VOC diffusion source

<table>
<thead>
<tr>
<th>trace gas</th>
<th>calib. source concentration [ppb]</th>
<th>protonated mass [amu]</th>
<th>thermal rate constant ([10^9 \text{ cm}^3/\text{s}])</th>
<th>PTR-MS concentration [ppb]</th>
<th>PTR-MS recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>9.65</td>
<td>m33</td>
<td>2.69</td>
<td>8.78</td>
<td>91</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>18.96</td>
<td>m45</td>
<td>3.74</td>
<td>17.60</td>
<td>93</td>
</tr>
<tr>
<td>acetone</td>
<td>31.36</td>
<td>m59</td>
<td>3.94</td>
<td>30.76</td>
<td>98</td>
</tr>
<tr>
<td>isoprene</td>
<td>5.39</td>
<td>m69</td>
<td>1.99</td>
<td>5.31</td>
<td>98</td>
</tr>
<tr>
<td>methacroleine</td>
<td>19.41</td>
<td>m71</td>
<td>4.06</td>
<td>15.60</td>
<td>80</td>
</tr>
<tr>
<td>methylvinylketone</td>
<td>4.67</td>
<td>m71</td>
<td>4.06</td>
<td>3.50</td>
<td>75</td>
</tr>
<tr>
<td>benzene</td>
<td>1.24</td>
<td>m79</td>
<td>1.92</td>
<td>1.09</td>
<td>88</td>
</tr>
<tr>
<td>toluene</td>
<td>0.31</td>
<td>m93</td>
<td>2.17</td>
<td>0.33</td>
<td>105</td>
</tr>
<tr>
<td>mixed monoterpenes</td>
<td>3.42</td>
<td>m81 + m137</td>
<td>2.00</td>
<td>2.58</td>
<td>75</td>
</tr>
</tbody>
</table>
In order to check the temporal stability of the PTR-MS performance, additional standard gas measurements were performed regularly using a multi-component cylinder gas standard (National Physical Laboratory, Middlesex, UK). The results for isoprene, toluene, as well as the sum of benzene, ethylbenzene, and xylene (that may interfere by fragmentations) are displayed in Figure 1a as recovery ratios relative to the nominal values of the cylinder standard. Between the beginning and the end of the ECHO field campaign, the apparent sensitivity of the PTR-MS decreased by about 40%. Since the SEM (secondary electron multiplier) of the instrument was already more than one and a half years old and was operated at a high voltage of 3300 V, the sensitivity drift may have been caused by a shift of the SEM response curve. Figure 1b illustrates this effect (for a newer SEM) in an exemplary way. The mass selectivity of the SEM is more or less constant in the upper part of the response curve but changes quickly at low voltages.

Fig. 1: (a) Time series of cylinder standard measurements by PTR-MS with constant SEM voltage of 3300 V; (b) SEM voltage dependence of PTR-MS signals: m19 source signal and ion count ratio m59/m19 for a constant acetone concentration.

Since mainly one significant drop in the m19 signal was observed in the middle of the measurement campaign (after a dislocation of the PTR-MS instrument), we assume that the general sensitivity drop was associated with that event and therefore we corrected the measurements for the second half of the campaign according to the cylinder standard calibration.

Fig. 2: Isoprene concentration at the top level of the forest tower (36 m above ground), simultaneous measurements by PTR-MS and GC-FID for two 4-day-periods at the beginning and the end of the field campaign.

4. Field Measurement Results
The following part is confined to some selected first results of the ECHO field campaign. Figure 2 shows isoprene concentration time series for the top of the forest tower as measured by PTR-MS and GC-FID. The second period was sunnier with generally higher temperatures. Isoprene that is mainly emitted by the local oak species Quercus robur shows a clear diel cycle following the solar radiation and temperature (not shown here) with largest values in the afternoon and low values during the night. The results of the PTR-MS and the GC-FID systems show a good agreement for both periods, yet with a considerable variability due to the non-synchronous sampling of the two analysers. Similar agreement was observed for other organic trace gases.

The contour plot in Figure 3 displays the development of the vertical isoprene distribution on 17 June, a clear and hot summer day. Beside the pronounced diurnal cycle of the isoprene concentration also shown in the time series plots, a distinct structure in the vertical profile can be observed. During daytime, the highest concentrations are found in the crown region and above the forest. However in the evening, the high concentrations seem to be mixed down more effectively into the lower part of the canopy. This effect might be due to a change of the in-canopy thermal stratification, which is often very stable during daytime and unstable during the night.

Fig. 3: Diel cycle of the vertical isoprene distribution within and above the forest canopy on 17 June 2002; the average canopy height of 30 m is indicated by the dashed line.

5. Conclusions

The PTR-MS with calculated concentrations was tested for a range of biogenic VOC’s using a laboratory diffusion calibration system. The agreement was within 25% or better, which is well within the expected uncertainty of the reaction constant k. However, an accurate determination of the instruments actual transmission function is essential since it can vary by more than 30%. The sensitivity drop of the PTR-MS during the ECHO field campaign was assigned to a shift in the SEM curve that caused the detector to work in the non-ideal mass-selective voltage range. The correction of this effect turned out to be successful because the comparison of the PTR-MS and the GC-FID time series showed reasonable agreement during the entire field campaign. The PTR-MS technique allowed fast measurements of four-level concentration profiles of various VOC species throughout the forest canopy at a time resolution of 20 minutes.

Acknowledgements

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References
Validation of Atmospheric VOC Measurements by PTR-MS

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PTR-MS has emerged as a useful tool for atmospheric chemistry studies. The technique allows several classes of volatile organic compounds (VOCs) from anthropogenic and biogenic origin to be measured along with some of their atmospheric oxidation products. The inherent fast response time of the measurement technique allows the monitoring of these VOCs with sufficient sensitivity and are especially useful in rapidly changing air masses such as encountered in aircraft measurements or when measuring close to emission sources.

In PTR-MS only the mass of protonated VOCs is determined, which is a valuable but not a unique indicator of the VOC identity. It is clear that VOCs with the same mass cannot be separately measured. Cluster ion formation and the fragmentation of product ions can lead to further mass overlap. In this presentation, we will show the results of recent studies, both in our laboratory and in the field, that were aimed at characterizing the response of PTR-MS towards several atmospheric VOCs of interest. In addition, we will discuss the development of a PTR-MS instrument with an ion trap mass spectrometer for improved capabilities of separating VOCs.

1. GC-PTR-MS analyses of urban air samples
In GC-PTR-MS, a gas chromatographic (GC) separation is used in combination with a PTR-MS instrument to distinguish the different VOCs that contribute to the signal at a given mass. Using this technique, we have analyzed numerous air samples by (1) trapping the VOCs in a liquid-nitrogen cooled sampling loop, (2) injecting the VOCs into a GC column, and (3) analyzing the column effluent with a PTR-MS. A typical result for some commonly used masses in PTR-MS is shown in Figure 1. The sample shown was collected behind our laboratory in Boulder Colorado and was heavily influenced by automobile exhaust.

The chromatograms in Figure 1 give a detailed insight into which VOCs are measured at the different masses. It is clear that the signals at masses 33, 42, 79 and 93 amu can be solely attributed to methanol, acetonitrile, benzene and toluene, respectively. The chromatogram for mass 45 amu shows two peaks due to acetaldehyde and CO₂. The catalytic converter that is used to determine the background signals does not remove CO₂, and thus acetaldehyde should be measurable without interference at 45 amu. The chromatogram at 59 amu shows two peaks due to propanal and acetone, respectively. The contribution from propanal is only significant close to pollution sources, and was never found to be more than 10% of the acetone response. The signals at masses 107 and 121 amu show several peaks attributed to the different C₈ and C₉ aromatic isomers, respectively. In addition, benzaldehyde is detected at mass 107 amu. As benzaldehyde is an oxidation product from toluene, its relative contribution to the signal at 107 amu increases with the degree of photochemical processing.
2. Comparison between GC-MS and PTR-MS measurements

The New England Air Quality Study (NEAQS) was conducted in the summer of 2002, and involved ship-based measurements of ozone, aerosols and their precursors along the east coast of the U.S. onboard the NOAA research ship Ron Brown. A PTR-MS was run side by side with a GC-MS instrument to characterize the role of VOCs in the formation of ozone and secondary organic aerosol in the region. The experiment also allowed a detailed quantitative comparison between the PTR-MS and GC-MS measurement techniques. Preliminary results for isoprene are shown in Figure 2. Panel A shows a part of both measurement series versus time. It is clear that the agreement between the two data sets is in most cases very good. Panel B shows a scatter plot of the PTR-MS versus the GC-MS data. It can be seen that below 100 pptv the agreement is substantially degraded, probably due to contributions in the PTR-MS instrument from other VOCs.

3. Separation of atmospheric VOCs by ion trap mass spectrometry

The use of a radio frequency ion trap offers analytical capabilities beyond those of the quadrupole mass filter used in the measurements described above. Ions of a single mass can be
collected in the ion trap and can be subsequently made to fragment in collisions with an inert buffer gas such as He. The resulting fragments can then be used to aid in identifying the initial ions. Another possibility is that the trapped ions can be made to react with a reactive VOC added to the He buffer gas. Different ions can thus be separated based on their proton affinity. In this work we have conducted an exploratory study to separate some common ions in PTR-MS using an ion trap mass spectrometer. Construction is underway of a PTR-MS instrument with an ion trap mass spectrometer for field studies.

Figure 3 shows an experiment in which protonated acetone (AC) from a complicated matrix of ions produced from water and acetone in a flowing afterglow (Panel A), is isolated in an ion trap (Panel B). Next, the kinetic energy of the trapped ions is enhanced using a filtered-noise field applied to the end caps of the trap. As a result the ion fragments at masses 31 amu, 41 amu and others are produced (Panel C). We have characterized the collision-induced fragmentation spectra of a number of protonated atmospheric VOCs. The results can be used to devise detection schemes for VOCs that cannot be separately measured using PTR-MS.

![Figure 3: Collision-induced dissociation of protonated acetone in an ion trap.](image)

The use of ion-molecule reactions inside the ion trap to separate ions is illustrated with Figure 4. In this experiment, protonated benzene and dimethyl sulfide (DMS) ions were collected in the ion trap and a trace amount of acetone was added to the He buffer gas in the trap. Protonated benzene reacts with acetone but protonated DMS does not. The results in Figure 4 were obtained by varying the trapping time and demonstrate that protonated benzene (at 79 amu) is gradually removed from the trap, whereas protonated DMS (at 63 amu) is not affected by the presence of acetone. Protonated acetone (at 59 amu) is formed in approximately the same amounts as the benzene removed. This approach can be used to separate different species that would otherwise be detected at the same mass in PTR-MS.
Figure 4: The use of ion-molecule reactions in the ion trap to separate different ion species.
Proton Transfer Reaction Ion Trap Mass Spectrometry and other PTR-MS Research at PNNL

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PTR-MS at the Pacific Northwest National Laboratory (PNNL) began in August of 2001 with the delivery of a custom-built PTR-MS instrument from Ionicon. The instrument was first used in an airborne gas and aerosol measurement campaign (PNW2001) was undertaken in Puget Sound from south of Seattle north to the Canadian border in a coordinated effort with the Canadian Pacific 2001 study. Since that time, application of the PTR-MS instrument has expanded to include measurements of VOC emissions from munitions, characterization of preconcentrators for solid-state sensors, and studies of pyrolysis in jet engine oil. There also have been related efforts using H₃O⁺ as a chemical ionization agent inside an ion trap mass spectrometer, comparing the results to charge transfer and electron impact ionization. Finally, in collaboration with Ionicon, the drift tube from the commercial PTR-MS has been coupled with a commercial ITMS instrument. We will present a summary of results from these current research areas as well as plans for the future.

For the PNW2001 campaign, the Battelle Gulfstream-159 aircraft (G-1) was used to measure meteorological parameters, ozone, ozone precursors, and aerosols. The objectives of the study were to better understand the transport and formation of ozone and particulate matter in the Puget Sound air shed and to develop air quality and meteorological databases for evaluating air quality forecast models being developed for this area. Figure 1 shows a time series of ozone and selected anthropogenic and biogenic precursor gases measured on the August 26th flight. PTR-MS measurements are shown in open symbols compared with canister measurements indicated by the closed circles. The PTR-MS was used to measure a dozen species with a dwell time of 1-2 seconds per mass, yielding a high temporal resolution database to better understand the spatial distribution of anthropogenic and biogenic species in Puget Sound. These results will be discussed in more detail.
The most recent effort at PNNL has been the interfacing of the Ionicon drift tube with an ion trap mass spectrometer (ITMS). This has been the subject of much speculation and discussion in the PTR-MS community. ITMS is appealing because of the ability to perform MS-MS and possibly distinguish between isomers and other isobars. There are, however, some serious questions, especially about the efficiency of injection of ions from the PTR-MS into the ion trap and the possibility of fragmentation. We have constructed a prototype instrument using an Ionicon drift tube and a Finnegan Saturn ITMS. A schematic is shown in figure 2. The interface is designed to replace the standard electron gun and uses a simple einzel lens focus the ions from the drift tube exit into the ITMS. The goal here was not to achieve the ultimate sensitivity, but to determine the efficiency of ion injection and to understand how to improve sensitivity in a second-generation instrument. We will also present some examples of MS-MS spectra. The design for an improved PTR-ITMS will be discussed.
Development of an APCI-MS to investigate surface processes of atmospheric trace gases

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ABSTRACT

To investigate the adsorption enthalpy, $\Delta H_{\text{ads}}$, of atmospheric trace gases on various ice surfaces, we developed a new instrument combining a chromatographic method and an Atmospheric Pressure Chemical Ionization Mass Spectrometer (APCI-MS). As an example, $\Delta H_{\text{ads}}$ of acetone is derived from its retention time measured through a column packed with a snow sample as function of temperature. The acetone concentration is monitored using proton transfer reaction and ligand switching reactions between water clusters and acetone.

1. Introduction

The photolysis of acetone is the main source of HO$_x$ in the upper troposphere [1]. Source and sinks of acetone need to be quantified to simulate the concentration of the main atmospheric oxidant HO$_x$. Partitioning to ice cirrus clouds is suggested to be one of the acetone sinks. Furthermore, snow-air and firn-air bi-directional fluxes of partially oxidized hydrocarbons such as carbonyl compounds and specifically acetone [2, 3] and their photochemical production in the upper snowpack [4-6] are significant enough to cause a strong impact on the carbonyl compounds concentrations in the planetary boundary layer, aging firns, and ice cores. However, the acetone mixing ratio between the gas and the solid phase is mainly determined by the value of its adsorption enthalpy. Thus, $\Delta H_{\text{ads}}$ of acetone on ice has been investigated by many authors and further measurements to validate its existing value are desirable.

2. The APCI-MS and the chromatographic method

The instrument is an Atmospheric Pressure Chemical Ionization Mass Spectrometer (APCI-MS, ABB Extrel, Merlin) housed in a two-stage differentially pumped vacuum chamber (Fig. 1). The APCI ion source is a corona discharge through which the acetone is carried by a 500 mL min$^{-1}$ flow of N$_2$ buffer gas (quality 99.999 %). Water clusters, H$^+$(H$_2$O)$_n$, formed from the trace amount of H$_2$O present in the buffer gas react with acetone in the APCI region (reaction 1).

$$H^+(H_2O)_n + (CH_3)_2CO \rightarrow H^+(H_2O)_{n-1}(CH_3)_2CO + H_2O \quad n \geq 1$$ (1)
The chromatographic technique to measure the adsorption enthalpy of atmospheric species on ice surfaces is similar to the one described in Bartels et al. [7]. The adsorption enthalpy ($\Delta H_{\text{ads}}$) of acetone (or any other non-reactive, non-diffusive, and non-dissociative atmospheric compounds) is directly derived from the measurement of its retention time ($t_R$) through a column (PFA Teflon) packed with ice as a function of the column temperature $T$ (200 - 240 K) [8].

$$\ln (t_R) = - \frac{\frac{a}{l} S_{ads}}{R} \left( \frac{1}{T} \right) + \frac{\frac{a}{l} S_{ads}}{R} - \ln \left( \frac{v A u}{l} \right)$$  \hspace{1cm} (2)

$l$ is the length of the column; $u$ and $v$ are the linear velocity and the volume of the gas in the column; $a$ is the surface area of ice; $A$ and $V$ are the standard surface area and volume of ice.

Introduction of acetone (and concentration calibration) is performed using a permeation tube (VICI, DYNACAL) housed inside a thermostated oven. Using a 4 port valve setup, the total flow through the column and the CI region remains constant (500 mL min$^{-1}$) whether if acetone is introduced or not through the column (Fig. 2).

3. Results and discussions

The retention time of acetone within the ice column $t_R$ is derived from the difference between the measurement of the total retention time within the complete system (Fig. 3; labelled plots with temperature values) and the measurement of the sum of the pre- and the post-column retention time (~2 ½ min) when the ice column is physically shortcut (Fig. 3; thick plot on the left part of the panel). Fig. 4 presents a plot of $\ln (t_R)$ versus inverse temperature measured from snow sampled in the top of Jungfraujoch (Switzerland, April 2002). The packed column is well characterized (inlet diameter: 0.6 cm; length: 66 cm; weight 7.5 g; Snow BET surface area: 206 cm$^2$ g$^{-1}$). An adsorption enthalpy ($\Delta H_{\text{ads}}$) of ($-56 \pm 3$, 2σ) kJ mol$^{-1}$ is derived according to Eq. (2). A comparable result is observed for polycrystalline ice spheres (~ ½ mm diameter) displaying a similar BET surface area. Since aging snow was used, its surface structure could be similar to that of the ice spheres and thus could lead to a similar $\Delta H_{\text{ads}}$ value. Indeed, it is suggested that defects on the ice surface have an effect on the calculated adsorption enthalpy of acetone on ice, implying higher $\Delta H_{\text{ads}}$ values for disordered ice surfaces than perfectly ordered ice surfaces [9, 10].
4. Conclusion and outlook

Our $\Delta H_{\text{ads}}$ measured on snow is in agreement with the ones derived by other authors on ice films within the same fractional coverage of one full monolayer ($0.01 \% < \theta < 3 \%$) and temperature range [11-13] and more specifically with the one obtained by Domine et al. [11] who also used the partition coefficient model to derive $\Delta H_{\text{ads}}$. Experiments are under way to compare the adsorption enthalpy of acetone between polycrystalline structures such as fresh snow, which should display higher surface defects than aging snow, ice spheres (poly-crystals), and single mono-crystal ice (no grain boundaries). Adsorption properties of other partially oxidized hydrocarbons could be also investigated.

5. Acknowledgements

We acknowledge L. Legagneux and F. Dominé (LGGE, Grenoble, France) who enabled T. Bartels-Rausch to the measurement of the BET surface areas of our snow sample and various ice surfaces. This work was supported by the Swiss National Science Foundation, the Swiss Federal Office of Education and Science and is integrated within the European Union project CUT-ICE n° EVK2-CT1999-00005.

6. References

1. L. Jaegle et al., Atmos. Environ. 35 (2001) 469.
7. Figures

Figure 1. The Atmospheric Pressure Chemical Ionization Mass Spectrometer (APCI-MS).

Figure 2. Schematic of the experimental set up (acetone flowing out of the ice column).

Figure 3. Retention time series \( t_R \) of the acetone within a column packed with a snow sample at various temperature. The reference time 0 is the moment when the acetone is introduced in the snow column following the \( \frac{1}{4} \) turn of the 4 ports valve drawn in Figure 2.

Figure 4. Plot of \( \ln \) (Retention time) versus inverse temperature for a column packed with snow.

\[ \text{Slope} = -\Delta H_{\text{ads}} / R \]

\[ \Delta H_{\text{ads}} = -(56 \pm 3) \text{ kJ mol}^{-1}, \ 2\sigma \]
Nitrous acid (HONO) measurements by PTR-MS

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Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a chemical ionization mass spectrometry technique that uses proton transfer reactions with H\textsubscript{3}O\textsuperscript{+} ions for real-time measurements of trace gases in air [Lindinger et al., 1998]. These reactions are almost invariably efficient for all compounds with a higher proton affinity than water being 165.0 kcal mol\textsuperscript{-1} [Hunter and Lias, 2001]. This criterion is met by the large majority of volatile organic compounds with the exception of small aliphatic hydrocarbons. We have expanded the PTR-MS technique to the measurement of gaseous nitrous acid (HONO), a volatile inorganic compound with a proton affinity of 187.7 kcal mol\textsuperscript{-1} [De Petris et al., 1982]. HONO is a key tropospheric species that acts as a source of OH radicals via photolysis. In the past 20 years a number of techniques have been developed for atmospheric HONO measurements but almost none has brought it to the stage of a sensitive real-time measurement device. PTR-MS allows for on-line measurements of HONO with a detection limit (S/N=2) of ~100 pptV at 10s- time resolution. The chemical ionization detection scheme for HONO was studied in detail using a Selected Ion Flow Drift Tube (Figure 1).

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {$\text{H}_3\text{O}^+ + \text{HONO} \xrightarrow{k = k_{\text{capt}}} \text{NO}^+ + \text{H}_2\text{O}$};
\node (b) at (2,0) {$\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{HONO} \xrightarrow{k = 0.9 \ k_{\text{capt}}} \text{NO}^+ \cdot (\text{H}_2\text{O})_2 + \text{H}_2\text{O}$};
\node (c) at (4,0) {$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2 + \text{HONO} \xrightarrow{k = 0.6 \ k_{\text{capt}}} \text{NO}^+ \cdot (\text{H}_2\text{O})_3 + \text{H}_2\text{O}$};
\end{tikzpicture}
\end{center}

\textbf{Figure 1} \quad \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{n=0,1,2} + \text{HONO} \text{ ion chemistry}

CID: Collision-induced dissociation
Due to CID processes in the PTR-MS flow drift tube the only major product of the \( \text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0,1,2} + \text{HONO} \) reaction is \( \text{NO}^+ \) (m/z=30).

The PTR-MS was calibrated for HONO using a continuous generation system for low-concentration gaseous nitrous acid \([\text{Taira and Kanda, 1990}]\) (Figure 2). The measured sensitivity was in excellent agreement with the calculated sensitivity which was derived following the usual procedure outlined in \( \text{Lindinger et al. [1998]} \).

Figure 2  PTR-MS calibration curve for HONO

The reaction of \( \text{H}_3\text{O}^+ \) with alkyl nitrites \( \text{R-ONO} \) yielding the \( \text{NO}^+ \) fragment and the heterogeneous formation of HONO from \( \text{NO}_2 \) (via \( \text{NO}_2 + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \)) on the inlet and drift tube walls were identified as potential interferences. Selectivity was, however, achieved by the use of a selective HONO scrubber (\( \text{Na}_2\text{CO}_3 \)-impregnated Nylon wool) which was periodically inserted into the analyte flow at the front end of the PTR-MS inlet system.

On-line measurements of HONO by PTR-MS were performed in the atmosphere simulation chamber SAPHIR (Forschungszentrum Jülich) and in ambient air at Jülich (Germany). The measurements were compared with data from a long path absorption photometer (LOPAP). The agreement with the well-established LOPAP technique was excellent (Figure 3).
Figure 3 Scatterplot of all PTR-MS and LOPAP HONO measurements during 6 days of experiments in the atmosphere simulation chamber SAPHIR with variable reagents: vaporized Milli-Q-water (0-11 mbar), NO (0-92 ppbV), O₃ and NO₂ (0-75 ppbV).

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2.2. Food Technology
Recent Research Using Proton Transfer Reaction Mass Spectrometry in Food Flavours, Plant Systems and Fragrances

Patrick J. Dunphy

ABSTRACT

Real time volatiles analysis imposes significant demands upon the analyst. The requirement to measure concentration in the range ppb-ppm for multi-component mixtures, of often unstable character, is compounded in the dynamic situation by the need for time dependent quantitation in the gas phase. These same demands of complexity and dynamics limit the use of classical work-up procedures and separation methods such as gas chromatography-mass spectrometry (GC-MS).

The utilisation of mass spectrometry in the CI mode permits direct analysis with concomitant generation of mostly simple spectra from complex volatile mixtures. Proton Transfer Reaction Mass Spectrometry (PTR-MS), the related Selected Ion Flow Tube (SIFT-MS) and Atmospheric Pressure Chemical Ionisation Mass Spectrometry (APCI-MS) fulfil the criteria for concentration and time management and in the case of the former facilitate direct quantitative measurement in the ppbv-ppmv range.

A review of recent literature will cover principally the application of PTR-MS in food flavours and plant systems. In addition this information will be supplemented by examples using APCI and SIFT drawing on fragrance and breath diagnostic studies respectively. These latter methodologies will help to illustrate the range of applications possible with these CI approaches.

This review will only consider the types of applications possible with these techniques in order to try to stimulate the adventurous flavour/fragrance scientist towards new understanding and opportunities.

Introduction

Classical methods of flavour volatile analysis such as gas chromatography-electron impact mass spectrometry (GC-EIMS) separate molecules by GC followed by partial ionisation of the individual molecular species from which identities can be deduced using appropriate databases. Such techniques give detailed structural information but are too slow to capture the temporal elements of flavour. In probing the flavour kinetics of complex mixtures the chromatographic element becomes a limiting factor. One solution is to replace the GC by MS both as the separation device and the detector. The prerequisite of ionisation for mass separation defines the necessity of soft ionisation for the resolution of complex mixtures. This is achieved by the application of chemical ionisation methods. The use of membrane interfaces (1) or jet separators (2) between the gas sample and the mass spectrometer have been applied but are limiting for complex mixture handling, differential species transfer and speed of analysis (3).

Three soft ionisation techniques are currently available, PTR-MS, SIFT and APCI, these producing mainly protonated molecular ions by a proton transfer reaction principally from H$_3$O$^+$ (4,5,6).

It is not the purpose of this review to compare and contrast these techniques but to consider the range of applications possible using these soft, direct, methods.

Applications of PTR-MS, SIFT and APCI.

The examples used in this talk were drawn from in vitro and in vivo systems.

In Vitro Studies

The nature of the system under evaluation defined principally the release vessel utilised. Model Maillard reactions based on skim milk powder and roasting coffee beans have been reported. For the former it was possible to follow the generation, release and identification of volatiles in a packed-bed reactor at initial moisture contents of 2.2 and 12.7g water/100g dry solid (7). Batch coffee roasting experiments were conducted on the small and large scale and the time intensity profiles of a large number of masses was monitored. Data alignment with the different physical stages of the roasting process and its transitions gave a direct insight into the complex chemical transformation occurring within the roasting bean (8).
Wound induced volatile organic compounds emission from plants represents a key element of the overall plant systemic defence response to mechanical and predator incursion. The virtually ubiquitous plant oxylipin system in leaf and other plant tissues represents a rapidly inducible complex system which enzymatically transforms non volatile fatty acyl lipids into odour potent volatile aldehydes, alcohols and esters (9). PTR-MS was employed to follow the rapid emission and further transformation of the initially formed (Z)-3-hexenal, within 1-2 seconds of wounding, in Aspen leaves. Employing the same technique parameters influencing the process including O₂ exclusion, extent of tissue damage and effect of tissue drying was evaluated (10). Similar studies were carried out using the CI method to monitor endogenous as well as wound induced volatiles release in garlic, onion and berry fruit. PTR-MS can also be used as a detector in the two dimensional mode by post-coupling to a gas chromatograph (GC-PTR-MS)(11). Maturation of commercially important berry fruit is similarly amenable wherein the volatiles released from fruit during the post-harvest stage of maturation were monitored over c.a. 6 days (12). The profiles of emission were fruit specific and diagnostic. Integration of this type of data with known plant physiology and biochemistry could provide routes to quality optimisation as well as providing support for the effects of exogenous parameters [temperature, controlled gas atmospheres (N₂, CO₂, C₂H₄)] on volatiles profile. Spoilage of meat stored at 22°C was monitored by the CI method tracking the generation of the aroma potent methanethiol and dimethyl sulfide; the former of which was produced rapidly, greatly on excess of its odour threshold, after c.a.28 hr (4). Strong correlation (about 99%) was observed between the microbial contamination and key volatiles emitted. Such rapid monitoring methods could replace time consuming (1-3 days) microbial colony development. This approach could similarly be applied to other fermentation processes.

Much has been written of the potential of electronic noses for the profiling of foods. Despite the promise much remains to be achieved especially regarding stability of the sensors and the limitation of the technique in compound identification. Seven different brands of Mozzarella cheese were profiled using classical sensory methods and headspace analysis by PTR-MS. The PTR-MS analysis was able to segregate the cheeses by type as did the sensory analysis. Comparison of the discrimination obtained by PTR-MS with that of the sensory analysis, showed clear similarities among samples between the two methods and good segmentation between samples (13). Further work is required to refine the sample presentation method and to link ion identity to sensory observations.

**In Vivo Studies**

**Human Breath Analysis**

Three main objectives of breath analysis monitoring are the evaluation of release profile “nosespace” of flavour during consumption of food, assessing metabolic transformation of ingested flavoured food materials and medical diagnosis of pathological condition.

- The evaluation of the release profile “nosespace” of flavour during consumption of food.
  
  Many studies have been conducted in this area for both fabricated and natural foods. The driving force being the assessment of the rate and profile of release of volatile compounds as affected by the environment of the mouth, the influence of food ingredients, particularly fat level, and the effect of product structure on the same. Important understanding can be derived from combining the analytical data with temporal sensory measurement and further consideration of the physical chemistry of the release processes involved. Data of this type has been derived for fabricated, O/W, emulsions where the effect of low fat in the presence or absence of encapsulating gel particles has been demonstrated (14). Consumption of a fresh whole strawberry exhibited a series of flavour temporal steps. These include an initial release of endogenous “fruity” esters along with other compounds that are released early but maximise later e.g. the “caramellic/strawberry” furaneol methyl ether. This is followed by the release of the induced “green” notes (Z)-3-/(E)-2-hexenal. Corresponding sensory data correlated well with the “nosespace” profile (15). This type of study provides “fresh strawberry” targets for the flavourist.

- Assessing metabolic transformation of ingested flavoured food materials.

The “cure-all” garlic clove is known to produce a whole family of mainly sulfur containing compounds that are reported to have significant systemic function *per se* and as a result of further transformation (16). PTR-MS monitoring of the metabolism of ingested raw garlic by breath analysis was carried out, for c.a.30 hr, following the fate of 8 sulfur compounds (17). The pattern of the components measured fell into two categories-diallyl disulfide exemplified compounds rising to a maximum shortly after ingestion with decline to baseline level after 2-3 hr whilst dimethyl sulfide, and acetone, increased much more gradually.
with maxima at 4-5 hr then a plateau (dimethyl sulfide) or declined more slowly (acetone). This elevation of acetone may reflect enhanced metabolism of lipids in the bloodstream and merits further study.

Medical diagnosis of pathological condition.

Breath testing diagnosis of pathological conditions has been an objective for many years in medical practice principally for the non invasive nature of the procedure. SIFT-MS has been applied to the analysis of ammonia, nitrous oxide, acetone, ethanol and methanol in the headspace of urine. Nitric oxide was found to be abnormally high in the headspace of acidified bacterially infected urine where nitrous acid was also detected. (18). Trace gas analysis of breath content of isoprene, acetone, ammonia, ethanol and methanol was performed during fasting and in response to feeding. The effects of the regimes employed were monitored for the volatiles named with different profiles being observed for each compound. Ammonia was of particular interest in exhibiting a biphasic response after feeding (19). Similar studies were conducted on the breath patterns of ethanol, acetaldehyde, ammonia, acetone and water vapour following ingestion of 500 ml ethanol (20). Previous work on schizophrenia has identified increased levels of carbon disulfide, ethane, pentane and butane in the breath of these patients (21). Medical conditions such as this may be amenable to probing by this non invasive method. In order to pursue diagnostic breath analysis for medical or environmental occupational exposure appropriate physiologically based pharmokinetic models need to be utilised to understand correlation between breath and blood levels of volatiles and to account for factors that can influence the blood to breath ratio (22).

Skin Monitoring

It is well accepted that the performance of perfumes on the skin of female consumers is perceived differently between individuals (23). This could be due to a number of factors among which are include their ethnicity and superimposed on this the dryness/oiliness of the skin. APCI has been applied to address at least the capability of measuring fragrance release from the skin surface in an intermittent mode initially and in addition monitoring fragrance release from simulated skin under dry and oily conditions. Real measurement as expected from a soap washed skin surface exhibited rapid release and poor persistence for small volatile molecules (e.g. ethanol) whilst alpha-isomethyl ionone persisted longer on the skin. On simulated oily skin the release profiles of indicator molecules changed significantly.

Volatiles Release from Living Flowers

Much recent interest has focused on capturing the fragrance of living flowers since they have been shown to differ both qualitatively and quantitatively from samples derived from petals by extraction. The focus of such activities was an analytical exercise to identify the key natural aroma compounds, latterly isolated by solid phase micro-extraction-gas chromatography, from the living plant (24). These and other methods are limited in that they only provide a snapshot of the floral fragrant environment when it is already well established that rhythmicity does occur during fragrance emission in many plants (25). Real-time monitoring was applied to follow scent emission from an intact, fully opened flower on the whole plant of *Jasmine officinalis* (family Oleaceae). Scent volatiles were continuously monitored over a period of c.a.110 min and the response of the flower to mechanical damage, approximately 85 min into the measurement period, was observed. Different release profiles for the constitutive compounds benzyl acetate, methyl salicylate and eugenol/isoeugenol were observed. Mechanical damage to the flower resulted in the transient formation of the wounding induced (Z)-3-hexenal. This technique would seem amenable to monitoring diurnal variation in fragrance release from flowers as well as the fragrance consequences of external interventions such as inhibitor and fragrance modifier addition.
Summary and Challenges

The development of CI methods clearly provides the capability for measuring quantitatively the real time profile of complex flavours and fragrances, in a multitude of situations, at levels commonly applied in flavoured foods and perfume systems. This capability provides the technologist with the opportunity to exploit these techniques to deliver optimised flavours and fragrances for a variety of application situations the dimensions of which are limited only by operator ingenuity.

Further improvements in these techniques could include refinement to increase selectivity and sensitivity. Two dimensional methods such as Resonance Multi Photo Ionisation (REMPI) with pulsed lasers coupled to Time of Flight Mass Spectrometers (REMPI-TOFMS), a combination of gas phase UV spectroscopy and mass spectrometry, represents a promising technique for chemical trace gas analysis. The approach combines sensitivity, selectivity and rapidity of measurement, with no sample preparation or chemical clean-up required, to achieve detection levels in the sub-ppb range even in the presence of highly complex mixtures. Further developments are awaited (26).

References


Model mouth analysis combined with Proton Transfer Reaction-Mass Spectrometry

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ABSTRACT
The dynamic release of five volatile flavor compounds from water and oil in a model mouth system was determined using Proton Transfer Reaction-Mass Spectrometry. The extent of release of the compounds from oil varied in intensity only. It followed the order of air/oil partition coefficients of the compounds and was related to the compounds’ hydrophobicity. The release patterns of the compounds from water varied not only in terms of intensity, but also in time to reach the maximum intensity, and increase and decrease before and after. As a consequence, proportions of the compounds varied with time. Increase in mastication rate increased flavor release, but the effect varied from 8 to 73% for the various compounds. Proportions, again, altered with mastication rate, which may result in a change of overall perception of the flavor mixture.

1. Introduction
The flavor of foods involves four different types of stimuli: aroma, taste, texture and mouthfeel. Perception of flavor is not simply an addition of the four basic stimuli, but a complex pattern that has different characteristics for particular foods. Aroma is the most diverse component of flavor, as the nose is capable of discerning hundreds of different odors. Thousands of volatile compounds contribute to the aroma component of flavor.

Several physico-chemical processes occur in the mouth when a food is consumed, which determine the release rates of volatile flavor compounds. Disruption of food material can lead to in-mouth generation of volatiles, mastication increases the surface area exposed to the air in the mouth, and hydration of foods by saliva affects flavor release as well. In order to study the release of volatile flavor compounds from foods under mouth conditions, mouth analogues have been developed. The authors presented their ‘model mouth’ in 1994 (1), and it considers a realistic sample volume, mouth volume, temperature, salivation, and mastication.

The release of volatile flavor compounds is not a static event. Its dynamics requires an analysis technique that allows fast real time measurements. Proton Transfer Reaction-Mass Spectrometry (PTR-MS; 2) is capable of these quantitative rapid measurements with high sensitivity. In the present study, the release behavior of five volatile flavor compounds from sunflower oil and water in the model mouth was examined using PTR-MS.

2. Materials and Methods
Solutions of 2-butanone, diacetyl, ethyl butyrate, hexanal, and 2-heptanone in sunflower oil and in distilled water were prepared in triplicate (0.001% v/v of each compound in oil and 0.0005% v/v in water).

Automated equilibrium headspace analyses were conducted on the oil and water solutions to determine air/liquid partition coefficients (3). With calibration standards, concentrations in air were calculated. For air/liquid partition coefficient calculations, the air concentrations were divided by the concentration of volatiles in the liquid phase.
For model mouth/PTR-MS analysis 10 ml of sample was placed in the model mouth according to the method described previously (4). A mastication rate of 26 or 52 rpm was employed, and no saliva was added. The headspace was drawn from the model mouth at 100 ml/min by a vacuum pump, 15 ml/min of which was led into the PTR-MS for real-time analysis (2). Data were collected for m/z 73 (2-butanone), 83 (hexanal), 87 (diacetyl), 115 (2-heptanone), and 117 (ethyl butyrate) once every 3 s for 0.5 s. Headspace concentrations were calculated as described by Lindinger et al. (2).

3. Results and Discussion

The air/liquid partition coefficients of the five volatile flavor compounds in oil and water were determined by equilibrium headspace gas chromatography (Table 1). The air/oil partition coefficients correlated negatively (r= -0.966) with the hydrophobicity of the compounds (log P, Table 1). The air/water partition coefficients were positively correlated with the log Ps (r=0.899). The correlation coefficients show that hydrophobic compounds have a higher affinity for the oil phase than the hydrophilic compounds, resulting in lower concentrations in the air phase, and consequently lower air/oil partition coefficients. The opposite phenomenon was observed for the compounds in water.

The dynamics of the release of the five volatile flavor compounds was studied in the model mouth using PTR-MS for real-time analysis (Fig. 1, Table 2). The release patterns varied both among the volatile compounds and the matrices (oil and water). In the oil, the order of intensity of the compounds was constant throughout the measurement period (12 min). This indicates that a compound high in concentration, such as 2-butanone, showed this behavior throughout. The release curves were relatively similar for the various compounds. The intensity of the compounds followed the order of their air/oil partition coefficients (Table 1), which implies that the thermodynamic component largely determined the volatile release. In contrary, the release dynamics of the various compounds in water varied considerably. Ethyl butyrate demonstrated a steep increase and decrease, whereas e.g. diacetyl showed a more gradual release. In the water matrix, obviously the kinetic component determined the flavor release to a larger extent than in the oil matrix. The time-dependent factor of release is important as when proportions of flavor compounds vary, the overall perception of a flavor may change during eating.

Table 1 Hydrophobicity (octanal/water partition coefficient: log P) and experimental air/liquid partition coefficients (K x 1000) of five volatile flavor compounds in oil and water (n=3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log P^a</th>
<th>Air/liquid partition coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>0.29</td>
<td>4.3</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>0.80</td>
<td>1.9</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>1.78</td>
<td>25.0</td>
</tr>
<tr>
<td>Hexanal</td>
<td>1.98</td>
<td>23.6</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>1.90</td>
<td>35.8</td>
</tr>
</tbody>
</table>

^a Lide, 1997 (5).
Fig. 1 Dynamic release of five volatile flavor compounds from water and oil under model mouth conditions determined by PTR-MS. Initial concentration of compounds in oil 0.001% v/v, in water 0.0005% v/v per compound.
The effect of mastication rates (26 and 52 rpm) on the release of the five volatile flavor compounds is presented in Table 2. Generally, maximum intensities increased with increase in mastication rate, although not proportionally. For instance, release of 2-heptanone increased only by 8%, whereas the release of diacetyl increased by 73%. Consequently, the proportions of the compounds varied with mastication rate. Larger proportions of the hydrophilic compounds (2-butanone, diacetyl) were determined with the 52 rpm mastication rate. The release of these compounds, and therefore their mass transfer coefficients, benefited more from the extra movements than their more hydrophobic counterparts. It implies that mass transfer is a determining factor for the release of these hydrophilic compounds from water.

Conclusions

PTR-MS was capable of real-time volatile flavor release measurements in the model mouth. The hydrophobicity of the volatile flavor compounds, the type of matrix, and the mastication rate employed, was shown to determine the dynamic release of five volatile flavor compounds.

References


Table 2 Maximum intensities of five aroma compounds released from oil and water in the model mouth using two mastication rates (26 and 52 rpm) determined by PTR-MS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water 52 rpm</th>
<th>Oil 52 rpm</th>
<th>Oil 26 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Butanone</td>
<td>6640</td>
<td>18943</td>
<td>12249</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>1651</td>
<td>5611</td>
<td>3236</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>18942</td>
<td>2033</td>
<td>1757</td>
</tr>
<tr>
<td>Hexanal</td>
<td>9833</td>
<td>1245</td>
<td>1043</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>9466</td>
<td>764</td>
<td>707</td>
</tr>
</tbody>
</table>

a Initial concentration of compounds in oil 0.001% v/v, in water 0.0005% v/v.
PTR-MS studies to assess and monitor fruit quality during preservation

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ABSTRACT
A PTR-MS study of the VOC emissions after different periods of preservation of apples and berry fruits will be reported. Several different systems were studied over the whole possible period of storage. Different varieties of apples, including Golden and Red Delicious, Renetta Canada, berry fruits such as strawberries and blueberries were investigated. The experiments included some low oxygen treatments (ILOS: internal low oxygen stress) before storage. A discussion will be given of the correlation between the VOCs emission observed in the headspace of the fruits and the effects on quality and preservation of the products. The impact of PTR-MS monitoring of these very important agronomic processes will be discussed.

1. Introduction
Flavours and aromas, which are the results of a complex mixture of many combined VOCs, are most important in both organoleptic quality and consumer acceptability determination of agronomical products and even of fruits. More than three hundred compounds have been observed in apple flavour profile (alcohols, aldehydes, ketones, esters)¹. Some are low concentrated and give a strong apple scent-flavour (for example ethyl2methylbutanoate)²; some others contribute to the aroma intensity (for example trans2hexenal) or are correlated to the aroma quality as ethanol³.

The understanding of the correlations between the VOC in the headspace of fruits is becoming of increasing interest for several different fields of research, food processing and

¹ Dimick P.S., Hoskin J.C., Review of apples flavor - state of the art, CRC critical review in food science and nutrition. 18 (1983), 386-409
marketing. Analysis of VOC emissions from apples and from many other agro industrial products is of great interest in terms of consumer acceptability and sensory characteristics of the product. In this context high sensitivity, fast and non destructive techniques have been improved through the last ten years and interesting results have been achieved both in gas-chromatography\(^4\) and in more innovative fields, such as electronic noses development\(^5,6\).

A more recent and significant contribution has been given by a new technique developed by Lindinger and co-workers\(^7\) which we applied to agro industrial issues and products such as apples, berries\(^8\) and cheeses\(^9\), with the co-operation of IASMA. As far as fruits is concerned a major topic of interest is to correlate the quality of fruits under different treatments and preservation methods in order to improve their quality and shelf–life at the market. This is particularly relevant to an alpine region as Trentino in Italy where the qualification of trade-marks is considered of major importance.

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\(^6\) T.Toccoli, S. Capone, L. Guerini, A. Anderle, A. Boschetti, E. Jacob, V. Micheli, P.Siciliano and S. Iannotta, Growth of Titanium Dioxide films by Seeded Supersonic Beams for VOC Sensing Applications, IEEE-sensors (in press)


We have investigated both different preservation and harvesting conditions for a series of varieties of apples and berry fruits. In particular we concentrated our efforts in evaluating the correlations between the VOCs emitted in the headspace of Renetta Canada, Golden and Red Delicious after different periods of conservation in standard controlled atmosphere and during a shelf life of a couple of weeks. The experiments concerned different post-harvest treatments such as 15 days of anoxia (ILOS) or chemical ethylene inhibitor such as MCP (methylcyclopropene) before the preservation period. Other subject of studies were the effects of different controlled atmosphere during the preservation period (i.e. low O₂ and CO₂ content). In the case of berry fruits the effects of different harvesting and preservation methods were also investigated. Here we only briefly discuss, as an example, the observations on ILOS treated Red Delicious apples. The experiments were carried out on two sets of apples one of which exposed for 15 days to an atmosphere composed by O₂ (0.5%) CO₂ (1.5%) at 1.2°C. The
standard preservation conditions were \(O_2\) (1.4%) \(CO_2\) (2.0%) at 1.2°C.

3. Results and discussion.

Figure 1 shows, in the left panel, the typical VOC emission at a selected number of masses at three different stages of preservation of the apples coming from the same cell. It appears evident that the emission intensity is very sensitive to the ILOS treatment. In particular the apples ILOS treated, at the observation after two months of preservation (top plot in the left panel), show much more intensity at some masses such as 43 amu, 45 amu, 61 amu and 89 amu while the opposite is observed at the other masses shown. It is very interesting to observe the evolution during preservation: two months later in the preservation period the intensities of emission were larger for the non treated samples for all the masse shown. This remains true even 2-3 months later. A way to assess this behaviour is to compare it with standard quality assessment by chemical-physical characterization (sugar, hardness, acidity) and combine quality index such as Thiualt. The corresponding values are reported for companion in the right panel of figure 1. The non treated samples seems to be better at the beginning of the preservation period while, later on, the chemical-physical characterization shows a better quality for the ILOS treated samples. We also analysed, using Laser Photoacoustic methods the ethylene emission and the results are shown in figure 2. The shelf-life evolution of the emissions shows that the apples during 15 days at room temperature will be undistinguishable.

If the data are treated by a statistical method based on the principal components

![Figure 5 Principal component analysis of the PTR-MS data of the same samples after 5 months of storage](image-url)
analysis that we developed one can easily determine how the PTR-MS VOCs data could discriminate the different treatments. Figure 3 shows one of such analysis for three observation during the 15 days of shelf-life of apples, ILOS treated and not, after a period of 5 months of storage. The square points correspond to the 1st day of shelf-life, circles correspond to 8th days and triangles to 15th days. The ILOS treated (full points) apples are discriminated already at the first day. During the evolution of the shelf-life the overall difference increases as the scattering of the points.
Rapid determination of the microbial spoilage of meat

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³Department of Plasmaphysics, Comenius University, 84248 Bratislava, Slovak Republic

ABSTRACT
We investigated the spoiling of air- and vacuum-packed meat (beef, pork and poultry) that was stored at 4°C for up to 13 days using Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS). We measured and identified partly the emitted volatile organic compounds (VOCs) as a function of storage time and found a large increase in these emissions after a few days of storage. Also a large difference in the spoiling behaviour between vacuum- and air-packed meat was observed.

2. Introduction
The aroma of meat changes during aging. In former times this was the only criterion for the human being to decide if the meat is eatable or not. This was crucial for his survival. The method currently used for determining the status of meat, with respect to spoilage, is to analyse the counts of total viable bacteria and/or specific spoilage bacteria. An obvious drawback of this bacteriological method is the long incubation period of 1-3 days that is required for colony formation.

In the present work we use the “old sniffing” method but instead of detecting the odour of the meat with the human nose we measure the VOCs by PTR-MS. We have measured the concentrations of several “spoiling compounds” in the headspace air of different kinds of meat that was stored at 4 °C. We compared beef, pork and poultry as well as the effect of different kinds of packaging (normal air versus vacuum). The goal of these investigations is to replace the time-consuming bacterial method by fast headspace air measurements to facilitate the investigation of a huge number of meat samples in very short time and to determine the remaining shelf life of meat during storage from the emissions. Such on-line measurements can also help to investigate the growth of different groups of bacteria, their activities and their metabolites produced in different surroundings (e.g. vacuum/air).

3. Experimental
Analysis of the VOCs
The method we used for analyzing the VOCs is a PTR-MS system. The PTR-MS and the corresponding measuring procedure has been described in detail in Refs. [1, 2]. For measuring the VOCs a small piece (about 15 g) was cut from the individual meat samples and was placed in a glass flask (300 ml) that was incubated at 25 °C. The headspace air was drawn at 114 ml/min by a vacuum pump, 14 ml/min of which was led through a heated teflon transfer line into the PTR-MS system for on-line analysis. The mass spectrometric data were collected over a mass range of m/z = 20–260 amu.

Performed Measurements
All meat samples were cut from the same piece of meat in a meat-processing factory, and each of them was separately packed and stored at 4 °C in a refrigerator. The emissions of 22 pork samples packed in normal air were measured one by one in the course of 13 days. Seventeen beef samples packed in normal air and 16 beef samples packed in vacuum were investigated in the same way for 10 days. An additional experiment was to measure the VOCs of vacuum-packed beef that was exposed to air after unpacking and incubation for 2 days at 25 °C after a storage time of 6.4 days at 4 °C.

4. Results and discussion
In a first set of measurements we investigated the emissions of the pork samples in the course of time. Typical spoiling compounds [3-6] detected on mass 89 (ethylacetate, methylpropionate, propylformate) are shown in Fig. 1. The concentrations started to exponentially increase after 3.5 days. After about 6 days the concentrations remained more or less unchanged. This behaviour of the emitted VOCs corresponds to a typical bacterial growth curve. An initial lag phase where the bacteria get used to the medium components is followed by an exponential increase in the bacterial biomass. After reaching a maximum, a stationary phase is obtained for a certain time before the number of bacteria decreases. We noticed the same trend in the emitted concentrations of many compounds like those shown in Fig. 1. Therefore, we conclude that bacteria produce these components.

In a second set of measurements we compared the VOCs emitted by beef under aerobic (normal packed) and anaerobic (vacuum-packed) conditions. The results are shown in Fig. 2. While the typical spoiling compounds ethylacetate, methylpropionate and propylformate (C4-esters) strongly increased with time in the case of the normal air-packed beef, the vacuum-packed beef showed a strong increase of ethanol. That confirms what we expected. Under anaerobic conditions (vacuum) mainly heterofermentative lactic bacteria are metabolically active and produce ethanol beside of lactic acid.

We measured also the VOCs of beef that was initially vacuum packed, stored for 6.4 days at 4°C, afterwards unwrapped and exposed to air for 2 days at 25 °C. What we can see in Fig. 3 is
that the ethanol concentration was strongly decreasing while the concentration of the C4-esters was increasing. It seems that aerobic bacteria (producing C4-esters) replaced the lactic bacteria (producing ethanol) with time. Nevertheless, lactic acid bacteria can also grow under aerobic conditions but stop ethanol production under these conditions.

Moreover, the present results indicate, that the emissions of pork and beef under aerobic conditions (normal air packed) are quite similar.

5. Conclusion
In the present work we have found that the time dependence of some VOCs emitted by spoiling meat appears to be similar to a bacterial growth curve. We have observed big differences in the emissions of normal air- and vacuum-packed meat, which result from different bacteria living under aerobic and anaerobic conditions with different metabolic activities.

![Figure 1](image1.png)

**Figure 1.** Concentrations of typical spoiling compounds (*)&: Sum of Ethyl acetate, Methyl propionate, Propyl formate, ■: Ethanol) emitted by normal-packed pork pieces that were stored at 4°C for a total of 13 days.

![Figure 2](image2.png)

**Figure 2.** Comparison of the emissions of normal air-packed (A) and vacuum-packed (B) beef in the course of time: The C4-esters (ethylacetate, methylpropionate, propylformate: *) are typical spoiling compounds emitted under aerobic conditions (normal air packed beef), and ethanol ( ■ ) is typically emitted under anaerobic conditions (vacuum-packed beef).
Figure 3. A vacuum-packed beef sample (previous storage time = 6.4 d at 4°C) was kept after a first measurement unwrapped in an open glass flask for 2 days at 25 °C, and emissions (☐: Sum of Ethyl acetate, Methyl propionate, Propyl formate, ■: Ethanol) were measured 6.5 and 49.25 h after the first measurement. Ethanol, the typical spoiling compound emitted by vacuum-packed meat, strongly decreased and the C4-esters increased.

6. Outlook
Encouraged by these results we measured the emitted VOCs of meat (beef and pork) using PTR-MS as a function of storage time. At the same time a bacteriological examination of these meat samples was carried out. We found statistically significant correlations between some of the VOCs and the bacteriological contamination. The analysis of the data is still in progress. The aim of these experiments is to replace bacteriological examination by fast measurements of the VOC concentrations in the headspace air of the meat sample to facilitate the investigation of a huge number of pieces of meat in very short time and to determine the maximum storage time and storage temperature from the emissions. We will also use this method to investigate the growth of various bacteria, the changes in the microbial composition and the influence of various environmental conditions such as temperature, pH, chemical and microbial preservation techniques. Furthermore, we plan to investigate the influence of bacteriological contamination on the aroma of various kinds of food.

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6. References
Discriminant analysis on PTR-MS data for agroindustrial applications

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ABSTRACT

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) data of agroindustrial products have been treated with a statistical analysis based on data compression of PTRMS spectra followed by class modelling. The examples discussed here indicate that this provides a fast and reliable method for product classification and quality control. In a first exploratory study 9 different strawberry clones measured 2-3 days after harvest were successfully distinguished by Linear Discriminant Analysis (LDA) of PTRMS data compressed by discriminant Partial Least Squares (dPLS). Moreover, samples of one clone collected at different times at different locations and cultivated in different ways are identified correctly in this way (14 correct identifications on 15 test measurements involving in each case one single, intact fruit). Similar analysis of PTRMS data for red orange juice allows a clear separation between thermal treated juices from fresh and high-pressure stabilised juice. In good agreement with results of discriminant sensory analysis, present PTR-MS measurements demonstrate that high-pressure treatment does not seem to have a strong impact on the volatile fraction of this juice.

1. Introduction

Authentication of food for origin, variety, defects etc. is an issue of extreme importance both for the producer and for the consumer and, up to now, no single analytical technique can completely address all the related problems. There are, at least, two main difficulties connected with quality control of food related products: (i) sensitive techniques (e.g. GC/MS) are usually expensive and not fast enough for continuos on-line application, and (ii) the high variability usually connected with food (vegetables, fruit, etc.) requires exploratory studies on several samples to understand if there are measurable attributes that distinguish, e.g., acceptable products from defected ones. Usually task (i) requires time consuming laboratory operations and is in contrast with the necessity of measuring several samples required for task (ii). Moreover the complexity of spectra obtained from very advanced spectrometric or spectroscopic techniques hardly allows simple data classification [1].

The problem of finding groups in data and/or sample classification has been addressed in many scientific areas (ranging from social science and econometrics to medicine and chemometrics) and various techniques have been developed. The availability of fast and cheap microprocessors opened the use of these techniques also for single users and small labs or factories.

In this work we describe how the interplay of fast PTRMS measurements with an appropriate data analysis based on data compression by Principal Components Analysis or discriminant Partial Least Squares followed by a suitable cluster analysis (Linear Discriminant Analysis or Canonical Variate Analysis) can give a powerful tool for the classification of agroindustrial products with the non trivial advantage of giving direct quantitative chemical information[1]. We will discuss here primarily the data analysis techniques (for more details on the experimental methods see the poster section and/or other publications [2,3]).
2. Material and method

2.1. PTRMS measurements

We discuss measurements obtained by a semi-static headspace method previously tested on several kinds of food products such as cheese, fruit juice, fruit, etc.[2,3]. In general the food sample is put in a glass container with a teflonated silicone septum and, after the time needed for the volatile compounds to reach equilibrium in the head space, we sample the head space by a stainless steel needle directly connected to the reaction chamber of the PTRMS via a heated (70°C, 1/8” O.D.) teflon tube. Pure nitrogen is injected into this container via another needle as buffer gas in order to avoid pressure drops. In most cases no dilution or concentration of the head space gas is necessary. Usually the measurements can be carried out fast enough to neglect the decrease in the signal due to the dilution with the nitrogen buffer gas. We skip 2–3 spectra taken at the beginning and take then the average of 3-5 spectra to characterise the samples. The present data analysis is performed on spectra normalised to unit area.

2.2. Data analysis

Mass spectrometric data are a typical example of a high dimensional data set, because the number of data are much larger than the number of desired results. In such a case it is useful to reduce the number of variates to be considered (data compression) to have simpler data visualisation and to avoid spurious effects connected with small random fluctuation (overfitting). Moreover some of the useful chemometric techniques apply only to data sets with a few dimensions [1].

In this contribution PTRMS data have been compressed by Principal Component Analysis (PCA) or discriminant Partial Least Squares (dPLS). Roughly speaking PCA tries to combine data to build new variates (called loadings) aiming at describing as much variance (information) in the first dimensions (no information on possible sample clustering is provided). In dPLS, on the contrary, the user indicates an assumed group to which each sample should belong and dPLS tries to build up scores to separate group centers as much as possible. Data compression is followed by Linear Discriminant Analysis (LDA, that is we attribute a single observation to the closest group) or Canonical Variate Analysis (CVA) [1].

In general, in view of applications in quality control, we have to test the developed model on a set of independent samples to check if they are attributed to the correct group. This can be achieved by dividing the data in a training set (serving as a model) and a test set (to check the model) or by internal cross validation: all samples serve as model and only one sample is used as a test case. The process is repeated for all samples in turn.

2.3. Samples

Strawberry: We consider two sets of samples: one comprises 3 fruits for each of 9 different varieties (indicated here by CS2, CS10, CS7, CS4, VR1, VR2, VR5, FB, PA) collected on the same day in the same field, the other comprises several fruits of CS2 collected in different places and different times to evaluate if our analysis is stable in time and robust with respect to different origin and cultivation systems.

Red orange juices: We investigated the differences induced by thermal (FP: flash pasteurisation and LP standard pasteurisation) and high pressure stabilisation (HP) on fresh red orange juice (FF). The corresponding samples from these treatments were three PET bottles of each type frozen after preparation and stored up to the measurement at -20 °C. About 12 hours before the PTR-MS analysis the samples (bottles) were immersed into a water-bath (10°C) to defrost the frozen juices. For details see [2].
We would like to note that in both cases, juices and strawberries, no pre-treatment, save for waiting for equilibrium in the head space, nor an external calibration has been performed.

3. Results and discussion

3.1. Strawberry

Fig. 1 shows the first three scores for dPLS of the PTRMS spectra of the 9 strawberry varieties (different symbols indicate different clone varieties). Even using only a few dimensions it is evident that a clear separation between the different clone varieties is possible. LDA can however be applied also to more dimensions and LDA on 10 dPLS scores gives in a cross validation test 27 successful identifications out of 28 test (96%). This is a very promising and interesting result because we achieve a correct variety identification with a non destructive, fast and easy measurement.

It is important to clarify whether the observed differences are due to the genetic and a real phenotypic expression of the different clones or are they attributable (having measured only on few samples so far) to differences in ripening degree, size, physiological and pathological conditions, etc.? To answer this question we use the second set of data for one variety (CS2) obtained for fruits collected at two different locations and at three different times and produced in two different ways (tunnel and open field). For equivalent fruits (4 days after harvest) 14 out of 15 test data are correctly attributed (93%). In fig. 3 hexagons represents the centres of 8 form the 9 groups of the first experiment, in contrast a large solid circle represents CS2 of the first experiment and small open circles represent these test measurements. Even in presence of the
maximum variability that we can expect from commercial fruits the model works robustly. Scores have been selected to have a good graphical display but it has to mentioned that 3 dimensions are not enough for proper attribution.

3.2. Red orange juice

Fig. 3 illustrates CVA for dPLS compression of the PTR-MS data for orange juices. FF: fresh reference product, HP pressure stabilised juice, FP soft thermal treatment, LP standard pasteurisation. Open symbols indicates training measurements, solid symbols designate the corresponding independent test measurements. Ellipses define 95% confidence regions. The relative good assignment of the test measurements to the correct groups should exclude overfitting of the data. It is immediately apparent that there exists a clear distinction between the untreated juice FF and the thermally stabilised juices FP and LP. These latter are also clearly separated. On the other side pressure stabilised juice (HP) is not significantly different from fresh juice (FF) and this is in agreement with sensory discriminative analysis: a panel of trained judges cannot distinguish between HP and FF.

4. Conclusions

We believe that the exciting properties of PTRMS (fast, sensitive, reduced fragmentation) coupled with suitable data analysis for data compression and class modelling can provide a tool to fill the gap usually found between highly sophisticated but time consuming analytical techniques and the real life applications where on-line measurements of several samples is necessary. Chemical information is also obtained and a further advantage of data compression is that loadings directly indicate the masses carrying the necessary information to separate different groups [2,3]. Here we reported results of only two examples, but we have indications that similar approaches work for other food products [3]. The proposed combination of PTRMS with discriminant analysis and class modelling provides a valuable tool for on-line, fast and sensitive monitoring of the quality, processes and products for factories, breeders, scientists, etc.

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Reference
Progress and Prospects of PTR-MS in Food Science

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ABSTRACT

In 1993, PTR-MS was reported for the first time in the literature. Since then the specifications of the technique have steadily improved. First, we would like to present the current status of the PTR-MS technique at the Nestlé Research Center. In particular we will discuss issues related to absolute headspace quantification, unambiguous chemical assignment and fragmentation. In a second part, we present two applications of PTR-MS from our research, which are particularly important to the aroma as perceived by consumers. This includes in-vivo aroma release from real food and model food systems (retronasal aroma), and studies on above-the-food aroma release (orthonasal aroma). Finally we will outline the prospects and possible role of PTR-MS for food research.

1. Introduction

PTR-MS for trace gas analysis is a young technique. Its first appearance in the scientific literature dates back to 1993, when Lindinger and co-workers published a paper entitled "An ion/molecule–reaction mass spectrometer used for on-line trace gas analysis" [1]. Besides fundamental studies on ion-molecule gas-phase reactions, W. Lindinger's attention was initially directed towards environmental and medical/health application [2-4]. It was not until January 1996 that we met W. Lindinger and his co-workers at the SAPS Meeting in Engelberg, Switzerland (Jan. 21-26, 1996). Realising the significance and versatility of W. Lindinger's work, we decided to collaborate in order to commonly projects in the field of food aroma. It was not later than February 13\(^{th}\) 1996 that we had the first PTR-MS headspace spectrum of a coffee brew. Figure 1 show on the front-panel the PTR-MS spectrum of air, while the back-panel shows a coffee headspace PTR-MS spectrum. These results showed that PTR-MS has the ability to detect a large number of volatile compounds released by e.g. a cup of coffee. Yet it also triggered a number of questions related to the interpretation of PTR-MS spectra.

- How important is the fragmentation of the ions upon ionisation by proton transfer in the drift tube?
- Are their interactions of volatile organic compounds with the inlet system and how can we "eliminate" these?
- How precise is the direct headspace quantification by on-line PTR-MS analysis, and what are the parameters to be considered to make PTR-MS a valuable tool for headspace quantification?
- Can we unambiguously assign the ion peaks of a PTR-MS to chemical compounds?

All these and other questions had to be addressed in order to get the best value out of PTR-MS. In a first part of our presentation, we would like to present the current status of PTR-MS from an analytical, technical perspective. In a second part we will discuss two applications that are particularly important to food aroma research.
2. Applications of PTR-MS in Food Aroma Research

Food aroma derives from interaction between aroma active volatile organic compounds and the olfactory epithelium in the upper part of the nose. In order to get a better understanding of the consumers perspective on food aroma, it is important to develop appropriate analytical methods that are capable of monitoring the dynamic aroma profile consumers are typically exposed to. Volatile organic compounds released from foods can reach the olfactory epithelium in the nose from two different directions. Either they are sniffed via the orthonasal pathway and enter the nostrils from the front. This aroma is associated with the above-the-food-aroma and corresponds to aroma perceived from a food product in front of a consumer. This is typically the case when smelling (sniffing) foods. Alternatively, when food is eaten and drunk, the aroma released in the mouth reach the olfactive receptors through the pharynx, via the retronasal pathway. Both these aromas are dynamic in their very nature, evolving with time and both are relevant to consumers. Here we will discuss two experimental approaches that attempt mimicking the orthonasal and the retronasal aroma release, respectively. Examples will be given for model and real food systems.

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We would like to thank W. Lindinger for his many contributions to our research.

3. References

Trace gas detection from fermentation processes

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ABSTRACT
Emission of various fermentation-related compounds like aldehydes, alcohols, acids and acetates released by rice plants and apples (cv. Jonagold and Elstar) under anoxic and post-anoxic conditions was measured on-line using a proton-transfer reaction mass spectrometer (PTR-MS).

In particular, the evolution of the fermentation products acetaldehyde and ethanol released by rice plants during the onset of fermentation and the transition period to aerobic atmosphere were simultaneously measured with PTR-MS and a CO-laser based photoacoustic detector. The gas emission measured by the two methods showed the same pattern. Due to its fast time response (< 1 sec.) and high sensitivity (sub ppb) PTR-MS allows obtaining detailed information on the kinetics of VOC's. Ethyl acetate and ethanol releases were strongly correlated in case of Jonagold apples, in contrast to Elstar apples where no correlation was found. Acetic acid released by Elstar was very high which is consistent with its tart flavor.

1. Introduction
Fermentation is the process by which the energy requirements of the cell are extracted from organic compounds without the involvement of oxygen. It continues the process of glycolysis, when the glucose molecule is broken down to pyruvate (Fig. 1). Thereafter, pyruvate may be converted either to lactate by the LDH enzyme (lactate fermentation) or to ethanol and CO₂ (alcoholic fermentation). The last one is a two-step process in which pyruvate is first decarboxylated to acetaldehyde (AA) by the PDC enzyme and subsequently acetaldehyde is converted to ethanol by ADH. At the onset of anoxia, LDH becomes active and lactate fermentation starts. The accumulation of lactate reduces the cytoplasmic pH, which inhibits LDH and activates PDC, leading to alcoholic fermentation.

Alcoholic fermentation occurs, for example, when plants are exposed to submergence [1,2] or in germinating seeds and pollen in relation with stress-signal transduction and disease-resistance.
response [3]. If O₂ is present, ethanol accumulated into the tissue can be metabolized to AA; this is consequently catalyzed by ALDH to acetate, which is further used in respiration.

Fermentation plays an important role in fruit storage. Typical controlled atmosphere (CA) conditions of 10% CO₂ 1% O₂ at 0 °C lead to reduced rate of respiration, suppressing the ripening and maturation. Under too low oxygen levels fruit switches from aerobic respiration to alcoholic fermentation [4]. Re-exposure to aerobic conditions induces a post-anoxic effect [5,6]. The study of physiological processes in fruit requires fast analysis of the concentration of the gases emitted. In addition, fruit releases numerous other gases contributing to the products flavor and aroma [7]. Knowledge is scarce on emission kinetics of these gases during rapidly changing of environmental conditions.

Therefore, we used a proton transfer reaction mass spectrometer (PTR-MS) to study fermentation on rice plants and apples. This instrument has proven to be a powerful tool for on-line monitoring of a large variety of gases of interest for environmental, medical and biological research [8-10] typically at sub ppbv levels (ppb = parts-per-billion, 1:10⁹). AA and ethanol emitted by young rice plants were simultaneously measured with the PTR-MS and a CO-laser based photoacoustic (PA) detector [11]. This laser-based detector has been used previously to investigate the dynamical aspects of fermentation in rice plants [12], red bell pepper [6] and avocado [13].

2. Experimental

The PTR-MS (see Fig. 2) consists of: (1) an ion source in which H₃O⁺ ions are produced in a H₂O-He mixture by a discharge, (2) a drift tube, where the trace gases from the gas sample are ionized by proton-transfer reactions with H₂O⁺ ions, (3) a collision dissociation chamber (CDC), where cluster molecules are dissociated, and a detection system consisting of (4) a quadrupole mass spectrometer and (5) an electron multiplier. Here, we will focus on the CDC, since it represents a novel part of the instrument compared to the systems reported in literature. The CDC is a transition chamber, where an intermediate pressure is maintained in order to reach a very low pressure in the detection region (10⁻⁷ mbar). It is pumped with a water-cooled turbo pump (210 l/s), which keeps the pressure typically at 10⁻⁴ mbar; at this pressure collision losses are minimized. In this chamber ion optics is used to compensate for misalignment of the ion beam and to focus on the entrance hole of the quadrupole mass spectrometer. In the drift tube clusters of gases and ions are formed with H₂O⁺ and/or H₂O. These clusters cannot be completely removed by increasing the voltage over the drift tube, because the collision probability decreases and subsequently the amount of protons transferred. In the CDC, the cluster ions can dissociate by increasing their
kinetic energy. In this way, they collide to other molecules and dissociate into a neutral part and the original protonized trace gas molecule. The neutral parts are pumped away by the turbo pump, while the remaining ions are lead towards the quadrupole entrance, where selection and detection of the ion takes place. The CDC was added to the PTR-MS in order to reduce the influence of the collisional induced dissociation.

The CO-laser based photoacoustic detector used simultaneously with the PTR-MS has an intracavity power up to 40W and is line-tunable over a large IR wavelength range, 5-8 µm. The detection limits achieved for AA and ethanol with this detection system is 0.1 ppb and 3 ppb, respectively.

3. Results

Acetaldehyde was detected at mass 45 (amu) and ethanol at mass 47 (amu). The measurements where performed with: pressure in the drift tube 2.47 mbar, the electric field over the drift tube 48 V cm$^{-1}$ and E/N =78 Td. The response of the instrument in ncp$s^{-1}$ is linear in the covered range (up to 1.2 ppmv for AA and 10 ppmv for ethanol). The sensitivity of the system is 72.5 ncp$s^{-1}$ ppbv$^{-1}$ and 21 ncp$s^{-1}$ ppbv$^{-1}$ both in nitrogen and air for AA and ethanol, respectively.

Three rice seedlings (14 days old) were placed into a closed cuvette and the gases released were transported to both the PTR-MS and the laser-based detector with a flow rate of 2 l/h for each detection system. The plants were placed in the dark and exposed for 2 h to anoxia (N$_2$ flow). Afterwards air was reintroduced (post-anoxia) and the evolution of the fermentation metabolites was followed during the first 2 h after transition to the aerobic environment. A typical response is shown in Figure 3. After 30 min of anoxia, an increase in AA and ethanol emission can be observed, showing that plant tissue switches from aerobic respiration to alcoholic fermentation. AA reaches a maximum of 625 ppbv after about 1 h, followed by a slow decrease, while ethanol increases steadily and reaches 13 ppmv after 2 h. Re-exposure to air resulted in a fast (10 min) outburst of AA of about 1500 ppbv. Thereafter AA emission rate decrease, reaching the initial aerobic rate after 2h of re-introduction of air. When the rice seedlings are re-exposed to air, ethanol emission rates start to decrease gradually to the initial pre-anaerobic emission rate.

Using PTR-MS other metabolic compounds related to anoxic and post-anoxic stresses in rice plants were also investigated (e.g. formaldehyde, propanal, butanal, pentanal, hexanal, acetic acid, formic acid, methanol and hexanol). Beside AA, ethanol and its drift tube reactions products (mass 29 and mass 65) only methanol (mass 33) was observed.

![Fig.3. Effect of 2 h anaerobic treatment (N$_2$ flow) and subsequent evolution of AA ethanol from 3 rice seedlings (14-d-old) measured simultaneously by PTR-MS (●) and CO laser-based PA detector (○).](image-url)
The study of the alcoholic fermentation and its related products was extended to apples. The emission of various gases under anoxic and post-anoxic conditions is shown in Fig. 4A for Jonagold. Under anoxia the emission of AA and ethanol started to rise already after 1 h. During the beginning of the anoxic period ethanol and ethyl acetate (mass 89) release both increased linearly with time as is shown in the inset (linear fit of first 9.5 h gives R=0.994 for both, N=286 samples). This observation is in correspondence with ref. [14] that showed that ethanol can be metabolized to ethyl acetate, the latter being the most prevalent of the variety of esters produced.

Switching from anoxia to post-anoxia yields only a moderate upsurge in AA (2-fold increase). Post-anoxic ethanol release remains high for a prolonged period, although it is known that ethanol can be metabolized at a rate up to 20 mg kg\(^{-1}\) d\(^{-1}\) if the O\(_2\) level is raised after an anoxic period [15].

Jonagold releases also a number of “heavy molecules” (mass 90-110) at quite high rates but unfortunately most could not be unambiguously determined.

In comparison with Jonagold, Elstar releases much more acetic acid (fig. 4B), which is in correspondence with the tart taste of Elstar and the mild sub-acid flavor of Jonagold. Under anaerobic conditions, acetic acid release is reduced as much as 75% in comparison with aerobic conditions. Under anaerobic conditions releases of ethyl acetate and ethanol are not correlated, in contrast to Jonagold and therefore ethyl acetate is possibly formed via other pathways. The post-anoxic upsurge in AA (3 fold) and the AA-ethanol ratio (2:9 after 16 hours anoxia) are both slightly higher than in Jonagold. Other volatiles released by Elstar include a number of alcohols (propanol, butanol, hexanol, and pentanol) and methyl acetate. Release of these compounds was reduced under anaerobic conditions (data not shown).

4. Conclusions

Using sensitive trace gas detectors, dynamic changing of AA and ethanol emission during the onset of fermentation and the transition to post-anoxia was monitored for rice plants and apples.

In order to achieve a high sensitivity in laser-based spectroscopy the wavelength of the laser has to coincide with a strong excitation band of the gas of interest. Therefore, only a few gases can
be detected simultaneously. PTR-MS is able to monitor a large number of VOC species at the same time with a higher time resolution (<1s) than photoacoustics.

Monitoring alcoholic fermentation products from rice plants with the PTR-MS shows a good agreement with the laser-based measurements, especially for AA. For ethanol, the laser detector showed a slower decrease of post-anoxic emission and about 2 times lower concentration as compared to PTR-MS. This can be explained by taking into account the memory effects caused by the long distance between the cuvette containing the samples and the PA system (about 5 m) and the tube used to transport the trace gas (nylon).

The fermentative behavior and its effects on the fruit quality were described for two apple cultivars. The measurements presented here show that application of sensitive monitors like PTR-MS and PA detectors in fruit storage opens new possibilities to gain insight in the kinetics of the relevant metabolic processes. Data can be used in many modeling studies.

References

A New Application of PTR-MS: Aroma Generation through the Maillard Reaction

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ABSTRACT
Proton transfer reaction mass spectrometry (PTR-MS) was applied to on-line monitoring of volatile Maillard reaction products. The formation of odorants was studied in model reactions containing reducing sugars (glucose) and amino acids (proline), which develop baked and popcorn-like flavours. Many of the odour-active components could be detected by PTR-MS, e.g. furaneol, acetic acid, diacetyl, and 2-acetyltetrahydropyridine. The kinetic curves give a particular insight into aroma generation as a dynamic process, adding a new dimension to aroma research. In addition, important volatile intermediates were detected, which represent major pathways in the Maillard reaction.

1. Introduction
In the last century, the major emphasis in aroma research was on identification and quantification of volatile compounds. Recently, work has been focused on those volatile compounds that show a sensory relevance in a given food system [1,2]. This was mainly achieved thanks to significant developments in gas chromatography (GC) coupled with mass spectrometry (MS) and olfactometry techniques. Although GC-MS was important to acquire knowledge on the nature and quantity of odorants, it does not allow studying dynamic processes during aroma generation.

So far, PTR-MS has been shown to be a suitable method for rapid and on-line measurement of volatile compounds in headspace samples [3-5]. It combines a soft and sensitive mode of chemical ionisation based on proton transfer from $\text{H}_3\text{O}^+$ with a quadrupole mass filter. The four key features of PTR-MS are as follows: (i) it is fast as time dependent variations of headspace profiles can be monitored with a time-resolution of about 0.1 s; (ii) the volatiles are not subjected to work-up or thermal stress and little fragmentation is induced by the ionisation step. Hence, mass spectral profiles closely reflect genuine headspace distributions, (iii) mass spectral intensities can be transformed into absolute headspace concentrations, without calibration or use of standards; and (iv) it is not invasive. All these features make PTR-MS particularly suited to investigate fast dynamic processes, such as aroma formation in Maillard reactions.

2. Experimental
Equimolar amounts of $\text{D}$-glucose (Glc, 0.1 mol) and $\text{L}$-proline (Pro, 0.1 mol) or the Amadori compound $\text{N}$-(1-deoxy-$\text{D}$-fructos-1-yl)-$\text{L}$-proline (Fru-Pro, 0.1 mol) were dissolved in a phosphate buffer (0.2 mol/l, 50 ml). After adjusting to pH 7, the solution was heated in a double-jacketed reaction vessel at 90°C for up to 5 h. Volatiles released into the headspace from Maillard model systems (80 ml) were monitored on-line by PTR-MS. The headspace (150 ml) was swept with a flow of nitrogen (5000 ml/min). An aliquot of the swept headspace gas (15 ml/min) was introduced into the PTR-MS for on-line headspace analysis. This high headspace sweep rate allowed the dynamic release of volatiles during the course of the Maillard reaction to be analysed. During the PTR-MS analysis the headspace gas is continuously introduced into the CI cell (drift tube), which contains air as buffer-gas and a controlled $\text{H}_3\text{O}^+$ ion density. Volatile organic compounds that have proton affinities larger than water (> 166.5 kcal/mol) are ionised by proton transfer from $\text{H}_3\text{O}^+$, and the protonated compounds are mass analysed. The CI-source
was specifically designed to reach high sensitivity and little fragmentation. To accomplish these targeted specifications, the generation of the primary $\text{H}_3\text{O}^+$-ions on the one hand and the chemical ionisation process on the other hand are spatially and temporally separating the generation of the primary $\text{H}_3\text{O}^+$-ions and the chemical ionisation process.

3. Results and Discussion

PTR-MS was applied to study dynamic changes in the headspace of Maillard reaction samples by simultaneously recording the temporal evolution of a series of mass intensities. The objective was twofold: (i) to study Maillard reaction samples based on sugar ($\alpha$-glucose, Glc) and amino acid ($\zeta$-proline, Pro) as compared to the corresponding Amadori compound (Fru-Pro) as a Maillard reaction intermediate, and (ii) to monitor not only the formation of volatile compounds that occur in high concentrations, but to focus on odour-active compounds contributing to the roasty and caramel-like aroma, which often are minor volatile constituents in the headspace.

As shown in Figure 1, 1-hydroxy-2-propanone (I) is one of the most abundant volatile reaction products that is readily formed from the Amadori compound (Fru-Pro) as compared to Glc/Pro. This observation is also valid for the three other volatile reaction products, thus indicating that the Amadori compound is more efficient in generating volatiles. As an example, the amount of compound II after a reaction period of 30 min was 10-times higher in the Amadori system as compared to Glc/Pro. In addition, the formation of II from Fru-Pro reaches a plateau after about 1 h, whereas it is continuously generated over 5 h in the reaction system Glc/Pro.

Furthermore, the formation of volatile reaction products from Fru-Pro is instantaneous, with the exception of 5-methyl-2-furfurylalcohol (III), which showed similar kinetic curves for both reaction systems. These data allow Amadori compounds to be seen as pre-reacted Maillard systems, which can rapidly generate volatile compounds by fragmentation reactions (I and II) or dehydration and cyclization (III and IV).

![Figure 1. Time-resolved monitoring of volatile Maillard reaction products from Glc/Pro (●) and Fru-Pro (■) at pH 7.](image-url)
As shown in Figure 2, also some of the odour-active Maillard reaction products could be monitored by PTR-MS, such as acetic acid \( V \) (acidic, pungent), 2,3-butanedione \( VI \) (buttery), furaneol \( VII \) (caramel-like), and 2-acetyltetrahydropyridine \( VIII \) (roasty). While \( V \) and \( VI \) were readily abundant, odorants \( VII \) and \( VIII \) were minor constituents in the headspace due to low reaction yields (\( VIII \)) or high polarity (\( VII \)), thus leading to low concentrations in the headspace. Their sensory relevance is due to low odour thresholds [2].

In general, the formation of odorants was favoured from the Amadori compound Fru-Pro, except of the roasty smelling \( VIII \) that was preferably generated from Glc/Pro. In agreement with that, the overall odour of the Glc/Pro reaction sample was described as mainly roasty and popcorn-like with a weak caramel-like note, whereas the Maillard sample Fru-Pro showed a strong caramel-like aroma and some roasty character. The caramel odour was mainly due to furaneol as evidenced by GC-O (data not shown).

It should be stressed that on-line monitoring of odorants such as furaneol (\( VII \)) and \( VIII \) is essential to gain insight into reaction kinetics, which explain temporal changes in the aroma character during the reaction. From the data shown in Figure 2, various overall aroma notes can be expected as the reaction is proceeding upon time. The data also indicate that odorant \( VIII \) is preferably generated through degradation products of Glc and Pro, i.e. 2-oxopropanal and 1-pyrroline, respectively, as described in the literature [6,7]. However, another roasty smelling odorant, 2-acteyl-1-pyrroline [8,9], could not be detected, most likely due to very low amounts.

PTR-MS data show that furaneol (\( VII \)) and 2,3-butanedione (\( VI \)) are almost instantaneously formed from Fru-Pro, thus indicating that the Amadori compound can, indeed, be seen as a pre-reacted Maillard system. Odorant \( VI \) goes through a maximum suggesting that it is rapidly formed but also consumed during the reaction, most likely by reacting with the amino acid and releasing the corresponding Strecker aldehyde [10]. On the other hand, acetic acid (\( V \)) is continuously formed upon time, thus explaining partly the decrease in pH, which is characteristic to Maillard reactions.

![Figure 2](image-url)

Figure 2. Time-resolved monitoring of odour-active volatile Maillard reaction products from Glc/Pro (●) and Fru-Pro (■) at pH 7.
In conclusions, PTR-MS was found to be a suitable method for monitoring volatile Maillard reaction products, even if they are very polar or occur in low concentrations such as key odorants with low threshold values. Thus, PTR-MS is suggested as an interesting on-line tool to study thermally induced aroma generation. These data can be rapidly obtained without any sample work-up. Further challenges in method development are expected in (i) increasing sensitivity (lower detection limit) to monitor odorants with very low threshold values and (ii) extending analysis to quantification for obtaining reliable quantitative results using water-air partition coefficients in dynamic headspace samples.

4. Acknowledgments

We thank Stéphanie Devaud, Walter Matthey-Doret, and Dr. Fabien Robert for the synthesis of the Amadori compound N-(1-deoxy-\(\alpha\)-fructos-1-yl)-L-proline as well as the reference compounds 2-acetyltetrahydropyridine and 2,3-dihydro-3,5-dihydroxy-6-methyl-4\(H\)-pyran-4-one. We are also grateful to Christian Lindinger for his contribution to the technical development of our PTR-MS equipment.

5. References


2.3. Medical Applications
Breath Monitoring of Propofol and its Volatile Metabolites in Real Time during Surgery using a Novel Mass Spectrometric Technique

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Until recently the use of soft chemical ionisation techniques for trace gas analysis of medical significance have been limited to large laboratory-based instruments, which are unsuitable for clinical use. This difficulty has been overcome with the recent development of a unique portable and low power apparatus, the proton transfer reaction mass spectrometer (PTR-MS).¹

We will demonstrate the use of the PTR-MS for drug monitoring; namely the intravenous anaesthetic propofol (2,6 di-isopropyl phenol) and its volatile metabolites (2,6 di-isopropyl quinone and 2,6 di-isopropyl quinol) on the breath of patients undergoing surgery. This illustrates the huge potential of using soft ionisation mass spectrometric techniques for the medical sciences.

Prior to any hospital trials, we established that the PTR-MS was capable of monitoring propofol at the low levels of concentration expected on the breath. This was achieved by sampling headspace air above serum taken previously from an anaesthetised patient. Figure 1 illustrates the mass spectrum obtained. A strong peak at 179 amu dominates, with weaker peaks at 95, 137 and 193 amu being distinguishable. The 179 amu peak is protonated propofol. The 95 and 137 amu peaks are also fingerprints of propofol, because they represent fragment ions resulting from collision-induced dissociation of the 179 amu ion in the PTR-MS, which was verified by selected ion flow tube studies performed by us, i.e. the masses at 95 and 137 amu do not result from dissociative proton transfer. The peak at 193 amu is the protonated quinone metabolite. These results were verified on the PTR-MS by sampling air above pure propofol. This provided a much greater signal to experiment with, so that masses could be readily identified.
**Figure 1:** Mass spectrum of the air sampled over serum taken from a patient anaesthetised with propofol. This spectrum represents the average of ten scans with the background subtracted. The peaks, which can be uniquely defined to propofol, are identified. The other mass peaks at 97, 101, 107, 111, 113, 115, 135, 139 and 141 amu remain unassigned.

All the patients in this study were anaesthetised using a standard continuous intravenous anaesthesia technique: induction using fentanyl (1-2 µg kg\(^{-1}\)), then propofol from a TCI device (set at 8 µg ml\(^{-1}\)) until loss of eyelash reflex, intubation facilitated using atracurium (0.5 mg kg\(^{-1}\)) and ventilation with a 50/50 O\(_2\)/N\(_2\)O mixture, muscle relaxation maintained with atracurium. During surgery, propofol was infused at a rate to deliver about 8 µg ml\(^{-1}\) plasma and gradually reduced to 4 µg ml\(^{-1}\) as surgery progressed.

For the hospital trials, a 4 m long unheated sampling tube conveyed the exhaled breath of an anaesthetised patient in surgery to the PTR-MS located in the adjacent anaesthetic room. The tube was attached immediately after a patient was taken into the theatre. Despite the considerable losses within our system, resulting mainly from surface adsorption on the sampling tube, we were still able to monitor propofol and its metabolites on the breath of patients. This illustrates that an intravenous anaesthetic can be monitored on a patient’s breath undergoing surgery. Whilst any conclusions are tentative at this stage, given the limited number of patients investigated, biological variation from one patient to the next was observed. More clinical measurements are therefore required if a specific correlation of propofol concentration injected
to propofol concentration on the breath is to be identified. Nevertheless, this could pave the way for the routine monitoring of propofol in a predictable manner.

Other applications of this soft ionisation technique, such as the non-invasive diagnosis and monitoring of diseases are planned.

Reference:

Acknowledgements
EPSRC provided a grant (GR/R06489/01) to purchase a PTR-MS. We thank Mr. S Arkless, School of Chemical Sciences, for his technical assistance. We are especially grateful to the medical and nursing staff in Birmingham Women’s Hospital NHS Trust for facilitating these investigations. We also thank the chairman of the South Birmingham Local Research Ethics Committee who gave approval for this study.
Breath Gas Analysis Using Proton-Transfer-Reaction Mass Spectrometry

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Physical, biochemical and molecular biological methods for medical diagnostics have been rapidly developing. Main focus has been laid on blood and urine diagnostics as well as on image analysis techniques. Diagnostics based on the patient’s breath, however, has been largely neglected so far.

Breath diagnostics is developed here with respect to 2 main lines of research:

1. Online breath measurements in the sleep lab, together with EKG-, EEG- and other parameters.

2. Measurement of breath VOCs (0-120 min) after a bolus of e.g. fructose with patients suffering from malabsorption syndrome.

Online measurements of breath allow the development of simple models for the impact of haemodynamics on VOC-concentrations. The measurements with patients suffering from malabsorption syndrome, on the other hand, give information on short-chain alcohols, aldehydes and carboxylic acids, which arise from bacterial metabolization of energy-rich substances (e.g. fructose, lactose) which are not absorbed in the intestines.
Analysis of Compounds in Human Breath: A New Approach in Cancer Detection and Risk Factor Assessment?

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Over the past decade, evidence has accumulated that certain patho-physiologic and metabolic processes may be mirrored by the composition of human exhaled air. Most notably, patients with lung cancer and hemato-oncologic disorders have been reported to feature distinct patterns of exhaled Volatile Organic Compounds (VOC). Phillips et al. and Rieder et al. conjectured orthotoluidine as a possible marker substance for neoplastic disease. It is the aim of the present talk to present applications of VOC screening in various patient collectives (end-stage renal disease, breast cancer, solid organ transplant, cystic fibrosis) and to review evidence on the potential role of VOC analysis in risk factor screening (hyperlipidemia, smoking, occupational exposure) using a Proton Transfer Reaction-Mass Spectrometer (PTR-MS). Furthermore, the gap to cellular processes is bridged by measurements of the VOC profile of various bacteria in vitro. In vivo, isoprene could be shown to increase during hemodialysis in patients with end-stage renal disease (ESRD). This has been ascribed to oxidative stress elicited by bioincompatible membranes, metabolic changes, and physiological parameters in connection with hemodialysis. Metabolic status of solid organ transplant patients, as mirrored by exhaled isoprene concentrations could be observed. Improved measurement techniques may possibly connect these features to transplant organ function and allow for non-invasive monitoring of these high-risk patients.

Risk factor assessment has been attempted in hyperlipidemia, in which elevations of isoprene may serve as a rapid screening marker, whereas increased levels of acetonitrile in exhaled air are indicative of recent smoking behaviour.

In conclusion, analysis of exhaled air by PTR-MS allows for rapid screening of large collectives for risk factors and certain potential disease biomarkers. Taking into account the rapidly growing number of publications into the diagnostic potential of VOC (see Figure 1), this sub-area in medical research is certain to increase in impact upon basic and clinical research.

Figure 1
3. Contributed Papers
Proton Transfer Reactions in Ion Mobility Spectrometry
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ABSTRACT
In this work the role of proton transfer reaction in ion mobility spectrometry, particularly in detection of volatile organic compounds has been stressed and a method for measurement of proton affinities by use of ion mobility spectrometry is described.

Introduction
Ion Mobility Spectrometry (IMS) is a rather new technology to develop small, portable and inexpensive analytical instrument for monitoring Volatile Organic Compounds (VOCs) such as alkanes, alcohols, halogenated hydrocarbons, aromatic hydrocarbons, halogenated aromatic hydrocarbons, halogenated biphenyls, carbonyl compounds (aldehydes, ketons, ether), phosphorous compounds and etc.1 IMS can analyze air, vapor, soil and water samples in less than a minute, with detection limits in the nanogram to picogram range, depending on the target analyte. This instrument has known to be the best for screening explosives at airports, detecting chemical agents for the military, and monitoring stack gas emissions in industry.2 A fast screening procedure for water samples contaminated with chlorobenzene was developed. The volatile organic compounds were purged from water samples and their concentration was determined with ion mobility spectrometry using corona discharge ionization.3 Due to its advantages, IMS has been used for monitoring air in the international space station to be sure it is safe for the astronauts at all times. In compare to mass spectrometry IMS operates at atmospheric pressure, therefore it doesn’t need large and expensive vacuum pumps and can be miniaturized easily. The principle of ion mobility spectrometer is based on time-of-flight measurement at atmospheric pressure. After a gaseous sample is entered into the spectrometer, the neutral molecules are ionized by electron or proton-transfer from reactant ions available in the ionization chamber to the sample molecules. A shutter grid allows periodic introduction of the ions into a drift tube, where they are separated base on charge, mass, and shape with the arrival time recorded by a detector. The ionization scheme in IMS for positive polarity is based on proton transfer reactions. Protons are generated either by radioactive sources such as $^{63}$Ni or by corona discharge.4 Since the carrier gas contains small amount of water (about 10 ppm) the ions are rapidly hydrated to form $(\text{H}_2\text{O})_n\text{H}^+$. Then the sample molecules are ionized via proton transfer reaction;

$$\text{(H}_2\text{O})_m\text{H}^+ + \text{M} \rightarrow (\text{H}_2\text{O})_m\text{MH}^+ + (\text{n-m})\text{H}_2\text{O} \quad (1)$$

The reactant ions $(\text{H}_2\text{O})_m\text{MH}^+$ remain hydrated during their migration in the drift tube. The difference between IMS and proton transfer reaction mass spectrometry is that in IMS water presents both in the ionization region and in the drift region. Thus compounds with proton affinities less than that of water cannot be ionized in IMS. When a mixture of analytes is introduced into the IMS, charge appears to be distributed proportionally to the individual vapor concentrations and proton affinities.

$$\text{MH}^+ + \text{N} \rightarrow \text{NH}^+ + \text{M} \quad \Delta\text{H}= \text{PA(M)}-\text{PA(N)} \quad (2)$$

The enthalpy change of this reaction is equal to relative proton affinity(PA) of M and N which can be measure through measuring the equilibrium constant as a function of temperature (Van't Hoff ploit). Then the relative proton affinity that plays an important
role in proton transfer reactions can be determined.

**Determination of relative proton affinities:**
The equilibrium constant for the proton transfer reaction 2 is:

\[
K_{eq} = \frac{[M][NH^+]}{[N][MH^+]} 
\]

In practice a fixed ratio of [M]/[N] was introduced into the ionization region of the ion mobility spectrometer by a peristaltic pump. Then the relative concentration of the two ions was measured while the pump flow rate was increased. At equilibrium conditions, the ratio [NH\(^+\)]/[MH\(^+\)] is expected to become independent of the flow rate if the ratio [M]/[N] is kept constant. At fixed ratio of [M]/[N], the ratio [NH\(^+\)]/[MH\(^+\)] is proportional to the equilibrium constant. Therefore, according to Van't Hoff equation, the plot of Ln([NH\(^+\)]/[MH\(^+\)]) versus 1/T gives the enthalpy change for the reaction.

**Results:**
Figure 1 shows the plot of the relative concentration of the two ions versus the pump speed for acetophenone and ethyl acetate. The reaction reaches the equilibrium conditions at about 15 µl/min. Experiments were performed at different temperatures as shown in Figure 2. The peak corresponding to the protonated ethyl acetate grows as temperature increases. Ethanol, ethyl acetate, cycloheptanone and were studied in this project. The results are in good agreement with other reported proton affinities. The results are also internally consistent.
Figure 1. The relative concentration of the two ions Acetophenon.\( \text{H}^+ \)/Ethylacetate.\( \text{H}^+ \) versus the pump rate. The ratio of the neutral reactants were kept constant.

Figure 2. Ion mobility spectra of a fixed mixture of ethyl acetate and acetophenone at different temperatures. The peaks E and A are the protonated ethyl acetate and acetophenone respectively and the peak D corresponds to the protonated dimer of acetophenone.

References:
Headspace of Grana Trentino Cheese measured by PTR-MS

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ABSTRACT
Headspace measurements of several samples of Grana Trentino cheese were performed by PTR-MS. We carried out an exploratory study on the emission of volatile organic compounds (VOCs) as function of the sampling position in the cheese loaf and on the influence of freezing the cheese before measurements. Sampling position turned out to strongly affect VOC emission; in contrast we did not notice a clear effect of freezing. In addition, a systematic study of the production of different cheese factories has been performed and we show the results of a multivariate analysis on preliminary data. Despite large difference between the VOCs for cheeses coming from the different locations, several masses have been identified to be directly correlated with the ripening degree. For ripened cheese mass 45 (mostly associated with acetaldehyde) is the most intense mass in PTR-MS spectra of Grana Trentino cheese as already noticed by Boscai et al.[1].

1. Introduction
The Proton Transfer Reaction - Mass Spectrometry (PTR-MS) method is more and more recognised as an important tool for the measurement of Volatile Organic Compounds (VOCs) and therefore it has been applied in several fields. Particular good performances have been achieved in the study of agroindustrial products [2,3,4] and based on previous promising studies [1,5] we carried out here a systematic study on Grana Trentino cheese. Here we report the results of this exploratory investigation. Grana Trentino, also known as Trentingrana, belongs to the Grana Padano family but it is identified by its own trademark. We expect large differences in flavour and VOCs associated with it, because this kind of cheese, even if controlled by a single consortium, is produced and stored in small cheese factories in different places ranging from the plain up to mountain (around 1000 m of altitude). Therefore the identification of common characteristics and quality markers is a tough task but can be of valuable economical and fundamental importance for quality control and trademark certification.

To develop a proper experimental procedure, we performed several tests to evaluate the effect of sampling different parts of the cheese loaf and of using frozen samples. After that we systematically measured, in parallel with sensory analysis, cheeses coming from 10 different cheese factories either being young (from 8 up to 12 months) or ripened (more than 18 months). This kind of study is of great interest because it could be the first step towards an automatic determination of cheese quality control based on fast, eventually on-line, measurements of VOCs. The possibility of correlating PTRMS data also with sensory profiles is a further intriguing issue.

2. Materials and methods
For the experiment on sampling different loaf positions a piece of cheese (radius 24 cm) of about 1 kg was divided into eight pieces, every single piece was then grated and this material was used for the measurements. For the further measurements twenty cheese loaves with different age (from 8 to 28 months) were obtained from ten different cheese factories in Trentino...
In these cases, from a piece of cheese of about 5 kg (height 10.5-11.5 cm, radius 20-24 cm, used also for sensory analysis) after the removal of the external layer (6 cm from the bottom, 4 cm from the external side and 3-4 cm from the tip), we cut a slice of about 2.5 x 4 x 12 cm. These slices were grated, well mixed and immediately used for the measurements.

Silicone-septum closed glass bottles of 120 ml (Supelco) containing 2.5 g of grated cheese (in triplicate) were placed in a water bath at 36.6 °C one hour before performing the measurements to assure equilibrium of VOCs between cheese and headspace. This headspace was then transferred through a heated (75 °C) capillary line directly into the drift tube of a commercial PTR-MS (Ionicon Analytik, Austria) at a rate of 10 sccm using pure nitrogen as buffer gas (SOL purity: 99.999%). The mass spectrometric data were collected over a mass range from m/z of 20 up to 260 amu using a dwell time of 0.2 sec per mass (in each cycle a complete mass spectrum up to mass 260 amu is monitored within a time span of 48 s). This sampling method has been tested successfully previously [4]. We measured each sample for 8 cycles, after starting the measurements we skip the first 2 cycles and then average the data of the next 5 cycles. The data collected were then converted in absolute concentration (ppb) according to Lindinger et al. [6].

3. Results and discussion

In the first experiment we measured the headspace formed above eight samples obtained from different parts of the same cheese. We studied here two extreme parts: internal (near to the core: NC) and external (near to the edge: NE, about 5 cm below the edge). For each sample we had a corresponding frozen sample to study the effect of freezing on the VOCs profile. Almost all masses have higher concentrations when measuring a sample from the external region. Among the most intense masses ( >1 ppb) only the concentration of mass 73 is higher for the internal region. This is probably due to the different ripening degree of the two extreme regions and in particular to the lower moisture of the external one. We found 41 masses that clearly distinguish (99% confidence) the two regions, 6 of them have a concentration above 100 ppb and 22 masses are ranging between 1 ppb and 70 ppb. This difference in VOC profile is a crucial point: in comparative studies we cannot just use any part of the loaf to make a comparison but we have to select one particular point for sampling. Alternatively (and we choose this way for further experiments discussed below) we need to mix cheese coming from different parts of the loaf. In contrast to the position, freezing and the following thaw seem not to have a great effect on the VOCs emission of the cheese. Only seven significant masses with low intensity were found to be different with a confidence of 99%. The most intense of these masses are mass 145 (ethyl hexanoate 21 versus 35 ppb) and mass 97 (heptanal 1.3 versus 1.6 ppb), all other discriminating masses (51, 155, 169, 139, 109) are below 1 ppb and further studies are necessary to confirm the effect of freezing on the related compounds.

After this exploratory study we measured cheeses coming from different cheese factories in Trentino. There is a great variety between the different cheeses mostly due to the production time, different ripening conditions and different point of origin.

Several masses are positively correlated with age, the highest correlation is for mass 42 (r = 0.76), mass 87 (r = 0.75), mass 85 (r = 0.70). Mass 42 is a fragment of an unidentified nitrogenous compound, mass 87 is the parent ion of 2-pentanone, 3-methyl-butanal and diacetyl, mass 85 is the parent ion of 2-nonanol. After analysis we divided the samples into two groups, a young one with an age of 8-12 months and an old one with an age of 18-28 months. We performed ANOVA on these two groups and found 11 significantly different masses (99.9% confidence), i.e., mass 45, 63, 65, 71, 75, 89, 103, 107, 115, 117, 145. Apart from mass 75 (propionic acid, ethyl propanoate), signals of all these masses are higher in the older cheeses. For young cheeses the total headspace concentration ranges between 10.3 and 18.4 ppmv, for old cheeses it ranges between 14.3 and 71.2 ppmv. The difference in headspace concentration is largely due to difference in the signal at mass 45.
We believe mass 45 to be acetaldehyde (the contribution of 3-methyl-butanal should be negligible and in general no other ion has enough intensity to justify such an intense fragment). Comparing cheeses coming from the same cheese factory we found that the mass 45 concentration in the headspace ranges from 0.52 to 2.63 ppmv in young cheeses and from 0.63 to 43.8 ppmv in old cheeses and is 5-60 times higher in the latter except for two cases in which this concentration in the older cheese is lower than the young cheese. Barbieri et al.[8], report a concentration, measured by enzymatic methods, of 0.57 mg of acetaldehyde per 100 g of cheese (5.7 mg/kg). Headspace concentrations of our samples could be compatible with these data if we take into account that a headspace concentration of 10 ppm of acetaldehyde is reached with a water solution of 6.16 mg/l (at 25 °C, Henry constant = 14 M/atm [9]). There is also an indication that mass 45 could be a marker for distinguishing between Grana Padano, Grana Trentino and Parmigiano Reggiano, as independently indicated by Boscaini et al. [1].

For old cheeses the most intense signals recorded with a concentration above 1 ppm are at mass 43 (common fragment in many compounds), 45 (acetaldehyde), 47 (ethanol), 59 (acetone), 61 (acetic acid), 89 (butanoic acid, ethyl acetate, ethyl butanoate, acetoine), for the young cheeses the most intense signals recorded with a concentration above 1 ppm are at mass, 45, 47, 59, 61.

Using the approach proposed by Kemsley for spectroscopic data [7] and tested also on PTR-MS spectra in our group [10] we applied to the present data a First Discriminant Analysis. The plot of the first two partial least squares (PLS) scores (see the figure above) shows a good separation of the two groups (young from ripened).

We checked this approach by performing a cross validation test using LDA (Linear Discriminant Analysis) on 3 PLS scores and the Mahalanobis distance [7]. We consider 2 classes (young and old). Every sample (except three samples having an age of 18, 23 and 23 months which were attributed to the young cheese class) were attributed to the correct class giving a success rate of 85%. It is not surprising that the 18 months old sample is attributed to the young cheeses because our separation limit (18 months) was quite arbitrary and, moreover, Grana Trentino is typically commercialised with an age of 18-24 months and older. Independent analysis will confirm if the misclassification of the two 23 months old samples can be justified independently.

Beside the intrinsic interest of multivariate approaches for quality control and product classification, they give also useful hints for chemical analysis. In the loading of the first PLS score we can immediately obtain an indication of the masses responsible for the observed differences and afterwards try to correlate these masses with chemical compounds. E.g. in the figure shown above the first loading of the reported PLS analysis clearly indicates the masses connected with ripened cheeses (negative peaks) and with young cheeses (positive peaks).
4. Conclusion

By PTRMS we can (i) measure the headspace of several cheese samples in a short time (much shorter than with a gas chromatographic techniques) without any pre-treatment of the sample apart from waiting for the headspace equilibrium, and (ii) obtain a ready fingerprint (mass spectrum) of the sample. The results obtained are not only limited to a simple classification/discrimination of the sample but information can also be obtained on the identification and quantification (of many) of the chemical compounds responsible for the differences within the samples. We have demonstrated here that we can easily monitor the ripening degree of Grana Trentino. Beside the absence of defects, the age (ripening degree) is one of the main factors to define the economic value of this cheese.

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References

Rapid Determination of Acetaldehyde in Cheese by PTR-MS

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ABSTRACT.
In previous PTR-MS flavour studies a high intensity at mass to charge ratio of 45 was observed to occur in the head space of ripened Grana Trentino cheese. This mass spectrometric signature (corresponding to the presence of acetaldehyde) could be an interesting feature both to distinguish this certified cheese from its direct competitors and to derive a measure to determine the ripening stage. In this contribution we show that based only on PTR-MS headspace measurements we can quickly and accurately determine acetaldehyde in cheese without any pre-treatment and using only small sample quantities. We first tested linearity and dynamic range of acetaldehyde detection using a water-acetaldehyde solution and than extended measurements to cheese samples. We also verified that the observed differences in headspace acetaldehyde can not be related to different humidity (ripening) or to matrix effects, but allows distinction between young and old (aged) cheese samples.

1. Introduction

Studying the headspace of Grana Trentino cheese we found an unexpected high signal at mass 45 for the most ripened analysed cheeses. This result is in good agreement with the data reported by Boscaini et al.¹ when comparing this cheese with similar competing products (i.e., Parmigiano Reggiano and Grana Padano). Mass 45 in PTR-MS spectra can usually be mostly related to acetaldehyde a common compound produced by the metabolism of micro-organisms used in the production of dairy products. In some fresh diary products a relatively large amount of acetaldehyde is required for a balanced flavor, while in ripened cheeses only relatively small amounts are expected². The usual methods used for acetaldehyde determination in cheese, i.e., enzymatic method (e.g. Boehringer-Mannheim, Milan, Italy) and simultaneous distillation extraction (SDE) are rather time consuming and involved, therefore it could be interesting to develop an alternative method, i.e., headspace analysis by PTR-MS, allowing a direct, fast and sensitive measurement without any sample pre-treatment.

2. Materials and methods

Acetaldehyde solutions. To test instrumental accuracy, linearity, and dynamic range, aqueous solutions with different concentrations of acetaldehyde were prepared and measured. A mother aqueous solution of acetaldehyde with a concentration of 1.0 g/l was prepared from a pure standard (Fluka) with distilled water. Further dilution allowed the preparation final concentrations ranging from 0.1 up to 50 mg/l. The solutions (15 ml) were placed in glass vials (20 ml). The headspace was drawn at 50 ml/min, 10 ml/min of which were led directly in the
drift tube of a commercial PTR-MS (Ionicon GmbH, Innsbruck, Austria). Measurements were performed in standard PTR-MS operating configuration and concentrations were calculated according to the method described by Lindinger and co-workers. We performed measurements for a sufficient time to reach a constant depletion rate in the headspace concentration thus allowing us to record an exponentially decreasing signal for mass 45. From the slope in a semi-log plot we can then calculate Henry’s constant \( H_e \) for acetaldehyde; we will call this dynamic method (DM). The used relation is:

\[
H_e = \phi \cdot \frac{1}{V} \cdot \frac{1}{R} \cdot \frac{1}{T} \cdot \frac{(\log e)}{\Delta}
\]  

Where \( \phi \) is the depleting flux, \( V \) the volume of the solution, \( R \) the gas constant, \( T \) the temperature and \( \Delta \) the slope of the recorded data for mass 45.

Another way to calculate the \( H_e \) consists in plotting the measured concentrations (expressed in ppb, \( v \)) in the headspace by PTR-MS versus the concentration (mg/l) of the prepared solutions and calculate the slope \( (\Delta) \) of the linear fit. \( H_e \) can be then obtained by formula (b). We will call this static method (SM).

\[
H_e = \frac{10^9}{44050} \cdot \frac{1}{\Delta}
\]

**Cheese mixed with water.** We prepared 5 vials containing about 200 mg of cheese (Grana Trentino with about 27 months ripening) and 10 ml of distilled water, into each vial we added 0.20, 0.81, 3.23, 24.12, 80.31 \( \mu g \) of acetaldehyde respectively obtaining increasing concentrations ranging from 0.40 up to 8.10 mg/l. With samples prepared in this way we obtained a calibration line which intersects the abscissa yielding measures for the concentration of acetaldehyde in the cheese sample only.

**Effect of humidity in cheese.** To evaluate the effect due to the water content in cheese (young and ripened cheese) or due to other matrix effects on headspace concentration of acetaldehyde we measured cheese under three different conditions: pure cheese, cheese plus water (1:1), and cheese plus \( \text{Na}_2\text{SO}_4 \) (1:1) to virtually eliminate water.

### 3. Results and discussion

Figure 1 (left panel) presents the PTR-MS determined concentration of acetaldehyde (molecular mass 44) at protonated mass 45 and its mono substituted \( ^{13}\text{C} \) and \( ^{14}\text{C} \) analogues at protonated masses 46 and 47 respectively. Solutions with a concentration above 8 mg/l are not considered here because being above the upper limit of the instrument (leading to a decrease in primary ion signal). We also did not consider solutions with a concentration below 0.1 mg/l because the systematic inaccuracies in the dilution stages affect the measurements. The fit in Fig.1 on these data shows a linearity across 4 orders of magnitude \( (R = 0.9999, \text{ slope } = 0.994) \) so it is possible to measure solutions with concentrations down to 1 \( \mu g/l \), the lower limit is due to the background. Using relation (b) for the SM we derive for \( H_e \) for acetaldehyde a value of 9.7 M/atm. Carrying out measurements according to DM we obtain for \( H_e \) for acetaldehyde using relation (a) a mean value of 9.9 \( \pm 0.2 \) M/atm. The good agreement between the two independent determinations of \( H_e \) confirms the accuracy of the present method.
Fig. 1: Left: Acetaldehyde headspace concentration at protonated mass 45 (stars) and its mono substituted $^{13}$C (circles) and $^{14}$C (squares) analogues measured in water/acetaldehyde solutions. Right: repeat measurements on different days and with different starting solutions.

The above data were confirmed in a second series of experiment and shown in the right panel of figure 1. The two series of repeat measurements carried out on different days (squares and circles) agree very well with each other and the results in the left panel thus indicating the good reproducibility of the method.

Analyzing the data form the cheese mixed with water sample (see the calibration line in Fig.2) a concentration of 0.136 mg/l of acetaldehyde was found, this corresponds to 6 mg of acetaldehyde per kg of cheese. Applying relation (b) we can calculate a repartition coefficient for acetaldehyde in the water-cheese system of $10.0 \pm 0.5$ M/atm, a value compatible with the $H_e$ calculated for the aqueous solution of acetaldehyde (9.7 M/atm).

Figure 3 shows that acetaldehyde emission is affected by the water content and/or the matrix, but this effect is smaller than the difference observed between young and ripened cheese.

Fig. 2: Intensity of mass 45 signal as a function of acetaldehyde added to a system of water (10 ml) and cheese (200 mg).

Fig. 3: Effect of water content in cheese on acetaldehyde headspace concentration. Young cheeses are indicated by Y (grey bars) and ripened cheeses by R (white bars): (R/Y) designate measurements with cheese only, (R/Y+H2O) with cheese/water mixture and (R/Y-H2O) with v, respectively.
A different way to estimate the total content of a compound in cheese is to follow its signal in time (during purging with a carrier gas) and than to integrate it. In fig. 4 we show that this gives a good linearity with respect to cheese quantity. Moreover we can estimate from the slope an acetaldehyde content in cheese of 2.5 g/kg in good agreement with literature values for similar cheeses.

4. Conclusions

We demonstrated that PTR-MS can accurately perform acetaldehyde determination in aqueous solutions over 4 orders of magnitude. We have also a strong indication that we can determine the acetaldehyde content in cheese from headspace measurements. Even if we do not have previous separation the contribution of fragments of other compounds to mass 45 can be assumed as negligible because we do not observe high enough signals at higher masses to indicate any appreciable contamination of mass 45.

The present method shows a better performances than the enzymatic methods and SDE under several aspects: no need of pre-treatments (critical for the very volatile acetaldehyde), very fast (few minutes) and the use of very small amount of sample. Another interesting point is that measurement of other interesting compounds can be performed simultaneously. This exploratory study will be continued compared with independent methods and possibly extended to other products.

Work supported by the FWF, Wien, Austria.

Fig. 4: Total amount of acetaldehyde in cheese as a function of cheese weight. By linear fit we estimate 2.5 g acetaldehyde per kilogram of cheese.
5. References

Measurement of CO, NO, NO\textsubscript{2}, Organic Compounds and PM\textsubscript{10} Particles at a Motorway Location during a Twelve Hour Blockade Period

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1. Introduction

Monitoring of automobile emissions in urban areas has become increasingly important in recent years, with air quality deteriorating as vehicle numbers have increased. This can have serious repercussions on health, with certain species having more adverse effects than others. Aldehydes, for instance, (which are produced directly by exhaust emissions and by photochemical processes) are an irritant for eyes and lungs, and benzene is known to be a carcinogenic agent [1]. Significantly, both aromatic hydrocarbons and aldehydes are produced by many industrial processes, being emitted from combustion sources, including automobile engines [1], with aromatic species such as benzene having long atmospheric lifetimes [2]. In addition to these, reactions of other species from vehicle emissions can have indirect adverse effects on health. It is well known that volatile organic compounds (VOC), in the presence of NO\textsubscript{x}, have significant impacts on oxidants such as O\textsubscript{3} and OH, with tropospheric O\textsubscript{3} being a recognised skin irritant. Oxidation of VOCs in these conditions has led to a drastic increase in O\textsubscript{3} in the planetary boundary layer (PBL) over the last one hundred years [3], which is not insignificant, given that fossil fuel combustion is known to dominate global NO\textsubscript{x} emissions. Particulate matter (PM) (especially that of anthropogenic origin, for instance from automobile emissions) is of particular concern, being a recognised catalyst in causing respiratory diseases, such as asthma, and cardiovascular disease (CVD), amongst other ailments [4].

Thus it can be seen that the monitoring of vehicle emissions is important in order to correlate these with health problems. To assess direct exhaust output, on-line measuring techniques are required, such that the transit time of air packets between emission and detection is minimised. Proton transfer reaction mass spectrometry (PTR-MS) (described in detail by Hansel et al., 1995 [5]) provides a means of monitoring certain compounds, offering a low detection limit and fast response time. The Innsbruck PTR-MS instrument was set up at the Vomp air quality monitoring station of the Amt der Tiroler Landesregierung, located within the River Inn valley (Tyrol, Austria). It is situated no more than two metres from the offside of the motorway hard-shoulder, making it ideal for immediate vehicle emission detection. The location itself has poor dilution conditions for air pollutants and high traffic and industrial sources.

The PTR-MS instrument was used to detect key chemical compounds in air in the vicinity of the motorway. These compounds included methanol (CH\textsubscript{3}OH), acetonitrile (CH\textsubscript{3}CN), acetaldehyde (C\textsubscript{2}H\textsubscript{4}O), acetone + propanal (C\textsubscript{3}H\textsubscript{6}O), benzene (C\textsubscript{6}H\textsubscript{6}), toluene (C\textsubscript{7}H\textsubscript{8}), plus higher mass aromatic hydrocarbons. The inlet was within 5 m distance from the motorway and was elevated approximately 2.7 m above ground level. Each compound was measured on a continuous cycle, with each run lasting just over one minute. In addition to these measurements, continuous monitoring of CO, NO and NO\textsubscript{2} was performed using a Horiba APMA-360 Ambient CO Monitor (using cross flow modulation, non-dispersive infrared [NDIR] absorption technology) and a Horiba APNA-360 Ambient NO\textsubscript{x} Monitor (using cross flow modulation type,
reduced pressure chemiluminescence [CLD]). Detection of PM$_{10}$ particles was also carried out with an Eberline FH 62 I-R Analyser.

Most significantly, measurements encompassed a motorway blockade, a period in which no vehicles were allowed to use that particular stretch of the motorway. The blockade began at 12 Midday on 25th October 2002 and lasted for twelve hours, ending at 12 Midnight. Monitoring of variations of the compounds outlined above was made throughout this period, with measurements beginning on 24th October and running through until 3rd November. This allowed assessment of variations during the blockade period of complete traffic absence and also over two weekends, where typically fewer vehicles were on the motorway.

2. Measurements
The PTR-MS inlet line was a 1/8", 5 m long PFA Teflon tube (flow rate ca. 500sccm), capped with a particulate filter. Table 1 below lists the masses detected by the PTR-MS and the corresponding names of the compounds.

<table>
<thead>
<tr>
<th>Mass (amu)</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>M33$^+$</td>
<td>Methanol</td>
</tr>
<tr>
<td>M42$^+$</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>M45$^+$</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>M59$^+$</td>
<td>Acetone + Propanal</td>
</tr>
<tr>
<td>M79$^+$</td>
<td>Benzene</td>
</tr>
<tr>
<td>M93$^+$</td>
<td>Toluene</td>
</tr>
<tr>
<td>M107$^+$</td>
<td>Sum: m-,p-,o-xylene, Ethylbenzene, Benzaldehyde</td>
</tr>
<tr>
<td>M121$^+$</td>
<td>Sum: Ethyltoluene, Trimethylbenzene, Propylbenzene</td>
</tr>
<tr>
<td>M135$^+$</td>
<td>Sum: Diethylbenzene, Tetramethylbenzene, Butylbenzene</td>
</tr>
</tbody>
</table>

Table 1. Masses and names of compounds detected by the Innsbruck PTR-MS

3. Results
Figure 1 shows the volume mixing ratios (VMRs) detected for each compound measured on Friday 25th October 2002, the day of the blockade; a) shows the minute averages for concentrations of CO, NO, NO$_2$ and PM$_{10}$ (in mg/m$^3$), b) displays concentrations for the organic species (PTR-MS, ppbV), and c) the aromatic compounds (PTR-MS, ppbV). The blockade began at 12:00 and ended at 00:00.

During the blockade period NO showed a dramatic decrease, falling to approximately 1% of its pre-blockade concentration (see Figure 1.a). CO and NO$_2$ also showed a decrease during this period, albeit less extreme, with levels dropping by about 50% for both. A less prominent drop was seen in the PM$_{10}$ particles, most likely due to their longer residence time in the surrounding air of the motorway. The aromatics (Figure 1.c) equally showed a concentration reduction throughout the absence of traffic. The organic species (Figure 1.b) showed little variation over the blockade period. It is interesting to note here the presence of a large peak in masses M45$^+$, M79$^+$, M93$^+$, M107$^+$, M121$^+$ and M135$^+$ amu at 08:21, with the M45$^+$ amu peak continuing for about two hours (until 10:22). This has been attributed to an as yet unknown industrial source.

Other peak events during the eleven day measurement campaign were also observed which, when related to wind data, showed non-vehicular origins.
Figure 1. Volume Mixing Ratios (VMR) of a) CO, NO, NO$_2$ and PM$_{10}$ (in mg/m$^3$), b) organic species, and c) aromatic compounds (both PTR-MS, ppbV), measured during the day of the motorway blockade (25$^{th}$ October 2002). The blockade began at 12:00 and ended at 00:00.
Principal components factor analysis was conducted on all compounds measured. The aromatics plus CO were all well correlated, clearly indicating a single source, with automobile emissions being the prime candidate. The other organics, plus NO\textsubscript{x}, were not quite as tightly correlated, possibly suggesting multiple sources.

4. Conclusions
The results from this measurement campaign indicate a strong correlation between traffic activity and the amount of NO in the air. Data also shows significant reductions of benzene and toluene in the air during the period of traffic absence. PM\textsubscript{10} particles showed only a minor decrease during the blockade period, presumably due to their longer residence time in air.

This measurement campaign has demonstrated that the PTR-MS instrument is an excellent device for conducting measurements that require a fast response time. It is ideal for monitoring automobile exhaust emissions in urban areas, which exhibit rapid variability of concentrations in such an environment. Combined with the CO\textsubscript{2}, NO\textsubscript{x} and PM\textsubscript{10} particle analysers, a whole range of data can be collected, allowing for detailed quantification of air quality.

References
Gas Chromatography-Olfactometry (GC-O) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS) analysis of the flavor profile of Grana Padano, Parmigiano Reggiano and Grana Trentino cheese

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ABSTRACT

Gas Chromatography-Olfactometry (GC-O) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS) techniques were used to deduce the profile of odor active and volatile compounds of three grana cheeses: Grana Padano (GP), Parmigiano Reggiano (PR) and Grana Trentino (GT). Samples for GC-O analysis were prepared by dynamic headspace extraction while a direct analysis of the headspace formed over cheese was performed by PTR-MS. Major contribution to the odor profile come from by ethyl butanoate, 2-heptanone and ethyl hexanoate with fruity notes. High concentration of mass 45 tentatively identified with acetaldehyde was found by PTR-MS analysis. Low odor threshold compounds e.g. methional and 1-octen-3-one contributing to the odor profile not detected by FID were detected by PTR-MS. Principal component analysis (PCA) on both GC-O and PTR-MS data allowed to clearly distinguish the three cheese samples and showed specific compounds related to each sample.

1. Introduction

Grana cheese is one of the worldwide known hard Italian cheeses, appreciated for its fruity and creamy flavor. Cheese with protected designation of origin has a high commercial value thus quality control and certification must undergo severe and reliable controls. Nowadays, controls on maturation and aroma are still carried out by expert people, checking and judging the stage of ripeness of the moulds one by one. In particular odor, derived from the volatile compounds in the headspace above the food, gives a first flavor impression and influences the acceptability and judgment of the food. The use of an automatic technique, which can reproduce the sensibility of human nose and can judge the quality of the cheese and link the cheese composition with its typical organoleptic features and original environment (1), could greatly reduce the check out time for the single moulds and probably reduce the costs of production. Two very interesting
techniques with rather high sensitivity and/or speed, which can be used for this purpose, are the Gas Chromatography-Olfactometry (GC-O) and the Proton Transfer Reaction-Mass Spectrometry (PTR-MS).

GC-O is a commonly used technique for analysis of odor active flavor compounds (2), which combines the capability of a capillary column to separate compounds with the high sensitivity of the human nose as a detector. A description of the odor can be given for each retention time corresponding to an odor active compound. Quantification can be carried out by a variety of methods, one of which is the detection frequency method utilizing a group of assessors (3, 4). The number of assessors detecting a specific odor active compound at the sniffing port at the same time (the frequency of detection) is used as a measure for the intensity of a compound. The high sensitivity, rapid time response, and the capability of performing absolute measurements of the PTR-MS (5, 6) have qualified this technique as an interesting alternative tool to obtain genuine headspace profile of real food. The volatile compound samples do not need to be prepared before the measurement, e.g. involving pre-concentration procedures, thus headspace sample over real food can be introduced directly into the reaction chamber. Interesting results were recently obtained in this sense for mozzarella cheeses (7) and red orange juices (8).

In the present study GC-O and PTR-MS techniques are applied to define the flavor profile of three certified grana cheeses: Parmigiano Reggiano and Grana Padano (PDO, protected designation of origin) cheeses and Grana Trentino (a Grana Padano brand produced in Trentino, northern Italy). These Italian hard cheeses are made from raw bovine milk, partly skimmed by creaming, with the addition of a natural whey starter, cooked at 53-55°C, and then usually ripened for 14–24 months (12). The place of origin, the cattle’s feeding, and the manufacturing protocol are the main factors determining the uniqueness and peculiarity of the cheeses.

Here the GC-O analysis is applied to identify the odor active compounds, utilizing an extraction by dynamic headspace in order to define the odor profile. With the PTR-MS analysis a real-time headspace profile is obtained, where no pre-concentration step is necessary thus no artifacts are introduced. Furthermore, the capability of the PTR-MS to detect low odor threshold compounds that are perceived by nose but are not detected by FID or by any other instrumental detector has been investigated here. The final goal of this work is to study the capability of GC-O and PTR-MS to distinguish between the three kinds of cheeses on the basis of their profiles of odor active and volatile compounds.

2. Results and discussion

A basic odor profile was obtained for each of the three cheeses analyzed. Fourteen compounds were present in the profile of Parmigiano Reggiano (PR) and of Grana Trentino (GT), while for Grana Padano (GP) there were 11 significant odor active components. Of the 19 characteristic
components totally found in the three cheeses, thirteen have been identified (Table 1). The three grana cheeses were characterized by fruity (ethyl butanoate, ethyl hexanoate, 3-methylbuthyl acetate, 2-heptanone, 3-methylbutanal), buttery-caramel (diacetyl), sulfuric (dimethyl sulfide), cooked-potatoes (methional), cheesy (2-methylpropionic acid) and mushroom notes (1-octen-3-one). Although ethyl butanoate, ethyl hexanoate, 1-octen-1-one, 2-heptanone and 2-methylpropionic acid appear to contribute to the odor profile of the 3 cheeses in a similar manner, nevertheless qualitative and quantitative differences existed between them. PCA performed on a combined sniffing chromatogram well illustrates the possible separation between the three cheeses and the related compounds of each sample (fig. 1). The diagram reveals three sites in which cheese samples and odor active compounds are closely related to each other. The following numbers refer to the compounds listed in table 1. Sweet notes (no 6 and 14), herbaceous (no 15) and glue/metal (no 8) odors correlated well with PR. Earthy/smoke, rancid, fruity/citrus, metal/sweet (no 7, 10, 11 and 13 respectively) correlated well with GT. Component 19 (metal/smoke) correlated well with GP.

A volatile profile defined by fifty masses resulted from the PTR-MS analysis of the three cheeses. The intensity of those masses ranged between 90ppb and 1ppm. Masses 45 (acetaldehyde, fragment of aldehydes), 59 (acetone, propanal), 47 (ethanol), 61 (acetic acid, fragment ethyl acetate), 43 (common fragment of many compounds), 89 (butyric acid, acetoin, 2-methylpropionic acid), 87 (2-pentanone, 3-methylbutanal, diacetyl) and 41 (common fragment of many compounds) were the most intense masses with concentration higher than 1ppm. Although all the masses were detected in the three cheeses, they showed different intensities and on this basis a clear separation occurs by the PCA of the quantitative mass spectra (fig. 2). The diagram reveals three sites in which cheese samples and volatile compounds are closely related to each other. Masses 75 (M75), 51 (M51), 115 (M115), 69 (M69), 71 (M71), 127 (M127), 45 (M45), 89 (M89), and 63 (M63) correlated well with GT. PR correlated well with M41, M87, M59, M33 and M157and GP with M93, M57 and M103. 

Table 1 Odor active compounds identified in the 3 grana cheeses and their detection frequencies (DF)

<table>
<thead>
<tr>
<th>no</th>
<th>Compound</th>
<th>LRI</th>
<th>Identification†</th>
<th>DF</th>
<th>Odor Descriptors (GCO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unknown 1</td>
<td>457</td>
<td>ni</td>
<td>GP</td>
<td>glue, smoke</td>
</tr>
<tr>
<td>2</td>
<td>dimethyl sulfide</td>
<td>526</td>
<td>MS, RI, GCO</td>
<td>3</td>
<td>sulfuric, earthy, rancid</td>
</tr>
<tr>
<td>3</td>
<td>2-methylpropionic acid</td>
<td>561</td>
<td>MS, RI, GCO</td>
<td>3</td>
<td>cheezy, earthy, caramel</td>
</tr>
<tr>
<td>4</td>
<td>diacetyl (t)</td>
<td>603</td>
<td>RI, GCO</td>
<td>5</td>
<td>caramel, sweet</td>
</tr>
<tr>
<td>5</td>
<td>3-methylbutanal</td>
<td>665</td>
<td>MS, RI, GCO</td>
<td>4</td>
<td>cheesy, herbaceous, mushroom, caramel</td>
</tr>
<tr>
<td>6</td>
<td>2-pentanone</td>
<td>711</td>
<td>MS, RI, GCO</td>
<td>2</td>
<td>Sweet</td>
</tr>
<tr>
<td>7</td>
<td>methyl butyrate</td>
<td>735</td>
<td>MS, RI, GCO</td>
<td>2</td>
<td>Fruity</td>
</tr>
<tr>
<td>8</td>
<td>unknown 2</td>
<td>741</td>
<td>ni</td>
<td>2</td>
<td>glue, metal</td>
</tr>
<tr>
<td>9</td>
<td>unknown 3</td>
<td>759</td>
<td>ni</td>
<td>6</td>
<td>sweet, fruity</td>
</tr>
<tr>
<td>10</td>
<td>pentanol</td>
<td>781</td>
<td>MS, RI</td>
<td>3</td>
<td>earthy, smoke</td>
</tr>
</tbody>
</table>
The GC-O analysis showed that the basic odor profile of grana cheese is a blend of 11 to 14 odor active compounds. The volatile profile of the same cheeses obtained from PTR-MS analysis is, as expected, more complex: 50 masses (parent and fragment ions) gave a significant contribution with at least 60 compounds tentatively identified. This shows that not all the volatile compounds in the headspace contribute to the odor profile of cheese as detected by the human receptors. In contrast all the identified odor active compounds were detected also with the PTR-MS, demonstrating its high sensitivity. Moreover PTR-MS was capable to detect two low odor threshold compounds like methional (mass 105) at 1-2ppb and 1-octen-3-one (mass 127) at 0.8 ppb, which give a high contribution to the odor profile of cheese although they are not detected by FID.

In conclusion, the capability of GC-O and PTR-MS to distinguish between the 3 kinds of Grana cheese on the basis of their odor and volatile profile has been proven and it is clearly demonstrated by the two PCA maps. Moreover the PTR-MS technique showed high sensitivity toward low odor threshold components, e.g. methional or 1-octen-3-one, that are difficult to detect with other instrumental techniques.

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**Reference**


Investigation of fundamental physical properties of a polydimethylsiloxane (PDMS) membrane using the PTR-MS

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²Pacific NW National Laboratory, Richland, WA, USA

ABSTRACT

The PTR-MS is utilized to investigate the dependence on temperature of physical properties, as diffusion and partition coefficients, of a silicon membrane. A combination of a membrane introduction system with the PTR-MS has been used for these experiments. Temperature increase showed large effects on rise time and solubility. Compounds having stronger interactions with the polymer, i.e. methanol and acetone, are more affected by temperature changes than non-polar compounds, i.e. benzene and toluene. The presence of methyl groups also seems to influence physical properties as diffusivity and solubility. The overall effect of temperature increase is to decrease diffusivity and solubility for organic compounds in air sample. Permeability data calculated from our experimental data obey the Arrhenius relation.

1. Introduction

Selective permeation through non-porous polymer membranes has been studied in the last decades as a more efficient method of separating fluids than distillation. Indeed energy requirements are lower, providing for lower overhead costs (1, 2). Glassy membranes are mainly used for recovering expensive gases (i.e. H₂, CO, H₂S) from synthesis purge gases or industrial gas stream. Whereas rubbery membranes due to their great permeability coefficient and hydrophobic properties are particularly suitable for dehydration of liquid organic solvents, water desalination, waste water treatment and food packaging. Due to these properties rubbery membranes have been found also another important application, i.e., as introduction system in mass spectrometry (MIMS, membrane introduction mass spectrometry) (3), with no danger to breach the vacuum and allowing batch or continuos sample introduction. The combination of membrane introduction system and PTR-MS has also been explored recently in our laboratory (4). The unique ability of the PTR-MS to measure absolute concentrations with rapid time response was used to demonstrate the possibility to measure certain fundamental properties of a PDMS membrane, such as solubility and diffusion coefficients. Moreover, a semi-permeable membrane was used to enhance the capabilities of the PTR-MS, i.e. elimination of certain isobaric interferences such as n case of acetone and propanal (both at m/Z = 59) or retention of water while making measurements in extremely humid environments.

In the present work the PTR-MS is utilized to investigate how certain physical properties of a Silastic™ (Dow Corning) tubing, such as diffusion coefficient (D) and partition coefficient (K), depend on membrane temperature. The permeation process through the membrane is
described by Fick’s diffusion equations (4), from which expressions for $D$ and $K$ are easily derived in eqs. 1 and 2:

$$\begin{align*}
1) \quad D &= 0.237 \left( \frac{t}{t_{10-90\%}} \right)^2 \\
2) \quad K &= \frac{F_{st} \cdot \ln \left( \frac{t_0}{t_f} \right)}{2\pi L D C_v}
\end{align*}$$

Permeation $P$, described as the product of $D$ and $K$, is a temperature-dependent phenomenon obeying the Arrhenius relation, eq. 3 (5):

$$P = P_0 \exp \left[ -\frac{E_P}{RT} \left( \frac{1}{1} - \frac{1}{RT_0} \right) \right] \quad \text{or} \quad \ln P = \left( \ln P_0 + \frac{E_P}{RT_0} \right) - \frac{E_P}{R} \cdot \frac{1}{T}$$

Direct measurements of steady state flow ($F_{st}$) and the rise time ($t_{10-90\%}$) for several species (methanol, 2.8ppm; toluene and benzene, 3.5ppm; acetone, 5ppm) are performed with the PTR-MS (for details of the experimental set-up see (4)). Values for $K$ and $D$ are calculated and compared to previous literature data. Values of permeability obtained with our experiments are verified to obey the Arrhenius relation.

2. Results and discussion

The temperature of the membrane inlet is one of the major parameters that influences the solubility and diffusivity of gases through polymers. Increasing the temperature the permeating gases have higher kinetic energy and thus they diffuse faster through the membrane.

The range of temperature chosen for the present investigation spans between 25°C and 65°C in order to avoid physical changes in the membrane, such as degradation at higher temperature or glassification at lower temperature. From the values of the rise time obtained experimentally, values for the diffusion coefficient ($D$) are obtained using eq. 1 (table1).

<table>
<thead>
<tr>
<th>Temp.[$°C$]</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>55</th>
<th>65</th>
<th>Increase factor</th>
<th>38*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.06</td>
<td>0.10</td>
<td>0.12</td>
<td>0.21</td>
<td>0.40</td>
<td>6.7</td>
<td>0.40</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.10</td>
<td>0.14</td>
<td>0.16</td>
<td>0.26</td>
<td>0.40</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.23</td>
<td>1.39</td>
<td>1.54</td>
<td>1.65</td>
<td>1.85</td>
<td>1.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.83</td>
<td>0.99</td>
<td>1.14</td>
<td>1.22</td>
<td>1.40</td>
<td>1.7</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 1 Diffusion coefficient ($D$) as function of temperature. *Sysoev et al. (6).

As expected the diffusion coefficient increases with temperature, moreover it’s observed that it’s smaller for acetone and methanol than for benzene and toluene. PDMS are hydrophobic membranes, which give strong interactions with polar compounds, i.e. methanol or acetone, and weak with non-polar compounds, i.e. benzene and toluene. Due to these interactions polar compounds diffuse much slower through the membrane than non-polar ones. However increasing the temperature the strength of these interactions decrease affecting much more the diffusion of polar than non-polar compounds; indeed the diffusion coefficient for methanol and acetone increases by a larger factor with the temperature than for benzene and toluene. It’s interesting also to notice that the values of $D$ for benzene are larger than the ones for toluene, indicating that toluene due to its methyl group interacts to a larger extent with the functional groups of the polymer than benzene. Previous data reported in literature show larger values for $D$ than ours. Sysoev et al. (6) found values of 4.8, 4.0 and 0.40 (x10^6 [cm²/s]) respectively for benzene, toluene and methanol at 38°C, no value are reported for acetone. However this
discrepancy might be explained due to different calculational methods used. Sysoev et al. considered as rise time the time required to achieve 50% of the steady flow using a theoretical fit while we considered rise time between 10% and 90% of the steady flow obtained from experimental data. Different was also the inlet mode utilized, in our experiments we used a flow over membrane inlet while a flow through membrane inlet was used in Sysoev’s. With this second kind of inlet it is easier to create an over pressure effect on the membrane yielding an expansion of it which reduces the thickness of the wall membrane, thus the rise time. Finally cooperation effects between the analytes might influence the diffusion, in fact with the PTR-MS we analyze multiple species at the same time while in Sysoev’s experiments one specie per time was measured.

The second consequence of increasing the temperature is the decrease of solubility of gases into the membrane. Increasing the temperature molecules in the membranes exhibit increased vibrational energies effectively occupying greater volume, which results in smaller free volume and lower solubility for gases. Moreover the partitioning of organic compounds into the membrane is reduced at higher temperature. The partition coefficient (K) is calculated from eq. 2, and is defined as the ratio between the activities (or approximately concentrations) in the stationary and mobile phase and it’s a measure of the solubility of VOC’s in the membrane.

<table>
<thead>
<tr>
<th></th>
<th>Partiton Coefficient, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. [°C] 25 35 45 55 65 Decrease factor 38*</td>
</tr>
<tr>
<td>Methanol</td>
<td>8018 4448 3411 1768 812 9.9 990</td>
</tr>
<tr>
<td>Acetone</td>
<td>4901 3203 2746 1443 811 6</td>
</tr>
<tr>
<td>Benzene</td>
<td>1165 935 765 601 458 2.5 220</td>
</tr>
<tr>
<td>Toluene</td>
<td>4061 3110 2361 1829 1326 3.1 560</td>
</tr>
</tbody>
</table>

* Sysoev et al. (6).

Table 2 Partition coefficient as function of temperature. Methanol (see table 2) showed the highest partition coefficient (or solubility) at room temperature among the compounds analyzed. Solubility of polar compounds like methanol in hydrophobic polymer as the PDMS might be favored by the affinity of the methyl groups present in both alcohol and polymer, and by hydrogen bonds between the hydroxyl group of the alcohol and the oxygen of the siloxane groups of the polymer. Toluene and acetone showed quite similar partition coefficients, in this case only the methyl group affinity might influence the solubility. It’s quite interesting to notice that the partition coefficient of benzene is more than 3 times lower than that of toluene, although they are both aromatic compounds. This shows that the substituent groups may play quite an important role in affecting the solubility. However this hypothesis should be confirmed by further studies where other substituent alkyl groups should be taken into consideration. The major solubility decrease is also observed for methanol. Interactions between polymer and analyte are weakened by the temperature increase, thus affecting to a major extent the solubility of those compounds having stronger interaction with the polymer. Sysoev et al. (6) measured distribution ratios in nitrogen gas (which is an analogue of the partition coefficient) as well, reporting values of 220, 560 and 990 for benzene, toluene and methanol at 38°C respectively. The discrepancy with our values might be attributed to the different calculation method of the rise time, over pressure and cooperative effect, as explained before. However the ratio between the three coefficients obtained from our data is quite similar to the one obtained from Sysoev et al.

Finally we want to check whether the experimental values of permeability obey the Arrhenius relation and therefore we plotted lnP (P= DxK) versus 1/T in fig. 1.
Figure 1 Logarithm of permeation is plotted versus $1/T$. The data are interpolated with a linear fit. The linear fit is in good agreement with the experimental data with regression coefficient of 0.99 for Toluene, Methanol and, Benzene and 0.97 for Acetone, confirming that the present data obey indeed the Arrhenius relation.

PTR-MS is confirmed to be a valuable tool to characterize polymeric membranes. The interesting results obtained from these experiments on the membrane will serve as an impetus for further studies especially on the effect of the alkyl groups on solubility and diffusitivity, and on characterization of new membrane materials.

**Acknowledgment**

Work partially supported by FWF, Wien.

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2) Mauritz – Diffusion Research. 2001 http\www.psrc.usm.edu/mauritz/diffuse.html


Measurement of trace gas emissions of spruce (Picea abies) by different techniques including PTR-MS at the BEWA field campaign 2002

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The capability of proton transfer reaction mass spectrometry (PTR-MS) [Lindinger et al.; 1998] for online measurements of volatile organic compounds (VOCs) such as isoprene, acetaldehyde, acetone, methyl vinyl ketone and metacrolein was used to measure VOC fluxes from spruce during the BEWA field campaign 2002. The BEWA measuring tower is located in the Bavarian "Fichtelgebirge", which has an alpine-like climate and is situated at 776 m a.s.l. at 50°09' N and 11°52' E.

A dynamic cuvette system was used for the measurement of trace gas emissions [Kreuzwieser et al.; 2002]. The cuvettes consisted of chemically inert teflon; one cuvette was kept empty as a reference; the plant cuvette contained a spruce twig of ca. 8 cm length at a height of about 13 m from the ground. The PTR-MS system continuously analysed all selected VOCs in the air from the plant cuvette over a 3 minute cycle, with measurement of the empty reference cuvette occurring every hour (Figure 1). Both cuvettes were flushed with ambient air at flow rates of 2-4 l/min. Emission rates were calculated taking into account the concentration differences between reference and plant cuvette, the air flow through the cuvettes and the leaf area of the twigs. In addition to PTR-MS, carbonyl concentrations were determined by DNPH-coated silica gel cartridges [Kuvata et al.; 1983] and subsequent HPLC-analysis. Simultaneously with trace gas exchange, the rates of photosynthesis and transpiration, stomatal conductance and meteorological parameters (PPFD, temperature, relative humidity) were determined. Depending on weather conditions the duration of one measurement cycle was up to 36 hours without interruption. In order to identify factors controlling trace gas emissions from spruce, correlation analyses of emission data with meteorological and physiological parameters were performed. Results obtained by cartridge and PTR-MS technique are compared for acetaldehyde (Figure 2).

As previously described for other plant species [see Kesselmeier and Staudt; 1999] exchange rates of VOC showed clear diurnal patterns with high emission rates during day and no /low emissions at night. A deposition of carbonyls was not detected in the present study. This is in accordance with laboratory studies in which spruce trees were able to take up carbonyls at ambient concentrations above ca. 6 ppb. Such high ambient concentrations, however, were not detected during the measuring campaign. In contrast to spruce, Mediterranean species seem to have lower compensation points around 1 ppb (acetaldehyde and formaldehyde; Kesselmeier; 2001) suggesting differences between Mediterranean species and spruce. Correlation analyses between VOC emissions and meteorological/physiological parameters indicated low correlation coefficients in the range of ~ 0.3 … ~0.6 (Fig. 4a and b) suggesting that either none of the factors studied affected VOC emission or that a combination of different factors modulated the emissions. For example, Figures 3a and b indicate an influence of both, irradiation and transpiration on the emission of acetaldehyde from spruce twigs. In the case of isoprene it is known that both temperature and light intensity determine production/emission rates (Kesselmeier and Staudt; 1999); the poor correlation between light intensities and isoprene
emission in the present study therefore may result from the influence of temperature. Preliminary studies during the field campaign in 2001 have shown that there is a good correlation between acetaldehyde emissions by spruce needles and the ethanol concentrations in the xylem of the trees; this result supports the hypothesis that xylem derived ethanol is oxidised in the leaves leading to the production and emission of acetaldehyde (Kreuzwieser et al.; 1999). It will be tested if such a correlation also exists for the data presented.

Figure 1. Measurement technique of the PTR-MS (e.g. for acetaldehyde): Every hour the reference cuvette was measured to take account of the changing inlet air and possible emissions from the cuvette material.

Figure 2. Comparison of the results obtained by cartridges (hour samples) and PTR-MS technique (high time resolution) for acetaldehyde.
Figure 3a and b. Influence of temperature, solar irradiation, assimilation and transpiration rates on the emission of acetaldehyde by spruce.
a. In the depicted period of time the dependency on solar radiation and transpiration rates can clearly be seen, while there is only slight variation in assimilation and temperature.
b. In another period of time the emission of acetaldehyde is kept high by an elevated temperature despite a decrease in radiation.
Figure 4a. Correlation of acetaldehyde emission vs. radiation

Figure 4b. Correlation of isoprene emission vs. temperature

References


Xylem-transported glucose as an additional carbon source for leaf isoprene formation in *Quercus robur* L.

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Isoprene is emitted from mature, photosynthesizing leaves of many plant species, particularly of trees (Kesselmeier & Staudt, 1999). Current interest in understanding the biochemical and physiological mechanisms controlling isoprene formation is caused by the important role isoprene plays in atmospheric chemistry. Isoprene reacts with hydroxyl radicals (OH) (Thompson, 1992) thereby generating oxidizing agents such as ozone and organic peroxides. Ozone causes significant deterioration in air quality and can pose threats to human health therefore its control is a major goal in Europe and the United States.

In recent years, much progress has been made in elucidating the pathways of isoprene biosynthesis (Kreuzwieser et al., 1999; Sharkey & Yeh, 2001). Nevertheless the regulatory mechanisms controlling isoprene emission are not completely understood. Light (Lichtenthaler, 1999) and temperature (Sharkey et al., 1996; Brüggemann & Schnitzler, 2002) appear to be the main factors controlling short-term variations in isoprene emission. Exposure of plants to \(^{13}\)CO\(_2\) showed instantaneous assimilated carbon is the primary carbon source for isoprene formation (Sanadze et al. 1972; Sanadze 1991; Delwiche & Sharkey, 1993). However, variations in diurnal and seasonal isoprene fluxes, which cannot be explained by temperature, light, and leaf development led to the suggestion that alternative carbon sources may exist contributing to isoprene emissions (Sharkey & Yeh, 2001).

The aim of the present study was to test whether xylem-transported carbohydrates act as additional sources for isoprene biosynthesis. For this purpose, [U-\(^{13}\)C] \(\alpha\)-D-glucose was fed to photosynthesizing leaves via the xylem of *Quercus robur* L. seedlings and the incorporation of \(^{13}\)C into emitted isoprene was monitored in real time using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS).

- A rapid incorporation of \(^{13}\)C from xylem-fed glucose into single (mass 70) and double (mass 71) \(^{13}\)C-labeled isoprene molecules was observed after a lag phase of approximately 5 to 10 minutes. This incorporation was temperature dependent and was highest (up to 13 % \(^{13}\)C of total carbon emitted as isoprene) at the temperature optimum of isoprene emission (40 - 42 °C) when net assimilation was strongly reduced.

- Fast dark-to-light transitions led to a strong single or double \(^{13}\)C-labeling of isoprene from xylem-fed [U-\(^{13}\)C] glucose. During a time period of 10 - 15 minutes up to 86 % of all isoprene molecules became single or double \(^{13}\)C-labelled, resulting in a \(^{13}\)C-portion of up to 30 % of total carbon emitted as isoprene.

- The results provide potential evidence that xylem-transported glucose or its degradation products can be used as additional precursors for isoprene biosynthesis and this carbon source becomes more important under conditions of limited photosynthesis.

Acknowledgement
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References


Measurements of VOCs in Tokyo urban area

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Sensitivity of the PTR-MS instrument is calibrated using standard gas for methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, benzene, toluene, xylene, and α-pinene. The humidity dependence of the sensitivity is also investigated. Because a primary $\text{H}_3\text{O}^+$ ion concentration increases with increasing humidity of sample air (20% increase for $\text{H}_2\text{O}$ mixing ratio of 3%), sensitivity of various species also increases. However when the sensitivities are normalized by the primary $\text{H}_3\text{O}^+$ ion concentration, a sensitivity does not change for acetone, while it decreases for benzene and toluene. This is likely because acetone reacts with $\text{H}_3\text{O}^+$ ($\text{H}_2\text{O})_n$ cluster ions, while the later two species do not react with cluster ions as reported by literatures. These humidity dependent sensitivities can be used for ambient air measurements. Samples of measurements in Tokyo are also presented.
Supervised Pattern Recognition applied to PTR-MS data: discrimination of strawberry cultivars

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ABSTRACT
Two supervised chemometric techniques (Discriminant Analysis – both Linear and Quadratic – and Artificial Neural Networks) have been used to authenticate the variety of 63 strawberry fruits, collected in different places and at different times, on the basis of their PTRMS spectra. The optimised models built using only the 2 most discriminating variables (m/z = 104 and 120), have been able to correctly predict 100 % of the samples as evaluated by a leave-$n$-out cross-validation procedure, with $n$ ranging from 1 to 6.

1. Introduction
The control, protection and evaluation of the quality of foodstuff is a matter of increasing importance both for the producers and the consumer. From the viewpoint of the food chemist, the term “quality” refers not only to the absence of adulteration or frauds, but also to the geographical or varietal origin of the product. While the detection of the frauds relies on the determination of peculiar chemical and physico-chemical fingerprints, at present no single analytical technique can be used to determine the origin of foodstuff.

During last two decades, the combination of chemometric methods with experimental analytical techniques resulted in the capability to ascertain the geographical and varietal origin of a wide set of foodstuff (e.g. olive or vegetable oils, wine, rice)[1]. Following up these earlier attempts, in the present work, two supervised chemometric algorithms (Discriminant Analysis and Artificial Neural Networks) have been used to analyse PTRMS spectrometric data for 63 strawberry samples from 2 cultivars (a commercial one and a selection, her “daughter”, under evaluation) in order to discriminate their varietal origin.

2. Materials and methods
The data sets comprise PTR-MS spectra in the region m/z = 20-260 of 63 strawberry fruits (31 from the "mother" variety and 32 from the “daughter”). Fruits have been collected at three different locations: a) in Cesena-Italy (tunnel cultivation), b) in Verona-Italy (open field cultivation) and c) in Cesena-Italy (open field cultivation). For each batch we measured 5-6 samples, single intact fruits, at the harvesting day and 5-6 samples after 4 days (3 days at 4°C and 1 day at room temperature). We measured single berries by closing them in a glass vessel
and sampling by PTRMS the headspace formed after 1 hour. Further information on those samples and on the experimental conditions for the PTRMS analysis are reported elsewhere [2]. Here we focus on the possibility of using pattern recognition techniques on these PTRMS data.

Discriminant Analysis and Artificial Neural Networks computation have been performed using the packages Statistica per Windows (StatSoft Inc., San Diego, CA), NeuralWorks II/Professional (NeuralWare Inc., San José, CA) and Lnknet for Linux (MIT, Boston, MS).

3. Results and Discussion

The PTRMS spectra, recorded for each sample, have been digitalized and organized in a matrix to perform subsequently the statistical analysis. Based on previous experience we normalised the spectra to unit total area before further analysis. This should reduce spurious effects: drifts, different fruit size and condition, experimental fluctuations, etc.

First of all, as including too much variables in the classification model could result in a poorer predictive ability, we tried to select the most discriminating masses by calculating the F-ratio [1]. F-ratio, defined as the ratio of between-groups to within-groups variance, is in fact a useful figure of merit to evaluate the discrimination ability of an experimental index. In table 1 we show the first 20 variables with the corresponding F value.

<table>
<thead>
<tr>
<th>m/z</th>
<th>F-ratio</th>
<th>m/z</th>
<th>F-ratio</th>
</tr>
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<tbody>
<tr>
<td>104</td>
<td>488.71</td>
<td>132</td>
<td>162.41</td>
</tr>
<tr>
<td>103</td>
<td>477.76</td>
<td>59</td>
<td>159.52</td>
</tr>
<tr>
<td>105</td>
<td>440.46</td>
<td>106</td>
<td>158.71</td>
</tr>
<tr>
<td>120</td>
<td>338.91</td>
<td>131</td>
<td>156.38</td>
</tr>
<tr>
<td>85</td>
<td>286.35</td>
<td>60</td>
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</tr>
<tr>
<td>41</td>
<td>281.13</td>
<td>118</td>
<td>140.96</td>
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<td>71</td>
<td>268.38</td>
<td>117</td>
<td>129.66</td>
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<td>121</td>
<td>238.98</td>
<td>149</td>
<td>115.12</td>
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<tr>
<td>122</td>
<td>188.47</td>
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<td>108.55</td>
</tr>
<tr>
<td>72</td>
<td>180.91</td>
<td>129</td>
<td>83.840</td>
</tr>
</tbody>
</table>

Several of these masses, being just different isotopes of the same compounds, are clearly strongly correlated: e.g. mass 104 and 105 are linearly correlated with mass 103, r > 0.99, with a isotope ratio compatible with a 5 carbon atoms composition. For the following treatment only the first of the correlated masses has been considered (mass 104 in the previous example).

On the basis of F-ratio values, we decided to retain only the minimum number of variables needed to achieve a 100% predictive ability, as evaluated by a cross-validation procedure. The use of cross-validation was suggested by the small number of samples (less than 100): it is reported in the literature, in fact, that for small data sets leave-n-out cross validation
(with \( n \) less than 10) is more accurate than a simple training/test set splitting to evaluate the predictive ability of the selected classifier. In this work, we have chosen to evaluate the performance of our classification models using a full leave-\( n \)-out procedure with \( n=1,2,4 \) and 6, so that the classification error be as independent as possible from the dimension of the validation folds.

The classification stage was performed using Discriminant Analysis (Linear and Quadratic) and Artificial Neural Networks. In Discriminant Analysis [3], the data from training set samples are used to build the \( g \) (\( g \) being the number of classes) classification function, one for each group; these functions are either linear (Linear Discriminant Analysis) or quadratic (Quadratic Discriminant Analysis) in the original variables. When an unknown sample is presented to the optimised classifier, the value of the classification function for each class is computed and the individual is assigned to the class which corresponds to the highest value of these functions.

In the present work, only two variables (intensity at \( m/z = 104 \) and 120) were needed to achieve a zero average prediction error in all the four cross validation experiments, both in linear and in quadratic discriminant analysis. As shown in figure 1 (left panel), where the projection of the data set onto the two selected masses is reported, the two cultivars are well separated and discriminated.

**Figure 1** – Data set projection onto the two selected variables (\( m/z=104 \) and 120); the “mother” variety data are represented as solid squares, “daughter” data as open circles. Left panel: normalised data used in further analysis; right panel: absolute data.

The use of the first variable only (\( m/z=104 \)) resulted instead of a zero average error in an average prediction error varying from 3.2\% (2 samples misclassified in leave-one-out experiments) to 7.9\% (5 samples misclassified in leave-six-out) when using LDA. With a single variable, using QDA resulted in a poorer discriminant ability, as the prediction error was ranging from 4.8\% (3 samples in leave-one-out) to 11.3\% (7 samples in leave-six-out).
Similar results have been obtained when using Artificial Neural Networks [4], i.e., a parallel distributed non-linear computational model, organized in three layers of independent processing units (nodes or neurons): each neuron of the input layer corresponds to an input variable presented to the network, while each output node produces an output value (in our case the probability that a sample belongs to a specific class); the neurons of the third layer (hidden layer) represent an implicit non-linear transformation from the input to the output hyperspace.

The optimisation of the network consists in using the training set data to adjust iteratively the numerical weights, which represent the strength of the connection from one node to another in a way that minimizes the root mean square classification error on those samples.

In the present work, for all the cross-validation experiments the weights have been initialised randomly and the training phase has been stopped when the rms error reached a minimum; to avoid the model from being stuck in local minima, random noise was then added to the optimised weights and training continued until a new convergence was reached.

Also in this case, only 2 variables were necessary to obtain a zero prediction error in all the cross-validation experiments and the optimised network had the structure:2-4-2. When using a single variable (m/z=104), the performance resulted better than in discriminant analysis, as only one or two samples in the validation folds have been misclassified.

4. Conclusions

The combination of PTRMS with chemometrics gives a promising approach to control quality of foodstuff. In the present exploratory study we used supervised pattern recognition techniques to demonstrate how this technique can easily discriminate between 2 strawberry cultivars, using only two variables. Besides this, further preliminary studies on the same data set show that, adding more variables to the classification model, it could be possible to distinguish between different production batches or different fresh fruits, i.e., from measurements on the harvesting day from stored fruits measured on the 4th day after harvesting.

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Development of a method for quality control of a herb extract

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ABSTRACT

We have developed an objective method for the determination of a herb extract’s quality based on headspace measurements by PTR-MS, while the quality was checked by a sensory analysis of the customer until now. This novel method enables the company X\textsuperscript{10} to check the quality of their product before selling it to customer Y\textsuperscript{10} and it also could be used for controlling and optimising the production process.

1. Introduction

Company X produces a herb extract in large amounts for a single customer Y. Before company Y buys the product it is checked by a sensory analysis. This check is the decisive factor for buying the extract. Since Y is the only customer, it is essential for the producer that the extract passes the sensory check. However, company X has no appropriate method for checking the quality of the extract itself and thus depends on the customer’s sensory judgement. In collaboration with X our aim was to develop an objective method which enables this company to control the quality of their extract before selling it to the customer. We measured the VOC concentrations in the headspace (HS) of 81 different batches by PTR-MS. Based on the sensory judgement of the customer we were able to find differences in the emissions of ‘good’ and ‘bad’ quality samples and developed a method for the quality control of this herb extract.

2. Experimental

We filled 2.5g of the extract in a glassware (radius=5cm, height=1cm) and equilibrated it in an oven at 30°C. Then we put the sample into a glass vial (radius=10cm, height=5cm) with a metal cover with two inlets for measuring the HS concentrations as shown in Fig. 1. We detected the VOC concentrations in the HS air of the extract samples on-line with an outdoor air flow of 14 sccm/min through the glass vial to the PTR-MS system. The mass spectrometric data were collected over a mass range of \textit{m/z} = 20–260 amu. Between measuring different samples we

\textsuperscript{10} Names of the companies changed because of duty to keep confidential.
switched on the pump of the bypass line to increase the flow through the Teflon lines in order to quickly reach the initial background concentrations. During the measurements the glass vial was placed in an oven to keep a constant temperature of 30°C. The lines to the PTR-MS were heated to 40°C.

Fig. 1: Experimental set-up to measure the HS of herb extract

3. Results and Discussion
During the last two years we received 81 batches (8 with ‘bad’ quality) of the herb extract and the corresponding results of the customer’s sensory analysis to develop a method for quality control. We measured the HS concentrations and tried to find differences between the ‘good’ and the ‘bad’ samples. A huge number of batches as well as a balanced ratio of accepted and rejected samples is necessary to develop a reliable quality control method. With a total of 81 batches and a ratio of 72:8 (accepted:rejected) we could not quite meet this ideal situation and, therefore, could not use any standard statistical methods to distinguish the important from the random differences between different quality samples. We had to develop different methods for finding the quality and often had to modify these methods after receiving further batches because the previous methods were not sufficiently general. Finally, we arrived at a method to analyse the PTR-MS data and to determine the quality giving satisfactory results for all samples available. The method is based on the measurements of 56 batches. Then we used this method to assign the quality of 25 further batches and compared our results with the ones of the customer’s sensory analysis and found perfect agreement.

We call this system “Hypothesis Generation”: We divided the batches into four different quality groups depending on the sensory description: ‘bad’, ‘okay’, ‘good’ and ‘very good’ (group number 1 for ‘bad’ to 4 for ‘very good’). Then we compared the concentrations (transmission corrected and normalized to the total ion counts (TIC)) averaged for each group 1-4 for each
detected mass. As an example Fig. 2 shows this procedure for mass 81. We found some differences in the emissions between the ‘good’ and ‘bad’ quality samples, determined conditions for the concentration on certain masses and calculated a “condition value” that enabled us to assign the consumer’s acceptability.

Calculation of the “condition value” (CV): 
\[ B^p = \sum_{i=1}^{n} K_i \theta (\varepsilon_i [C_{m_i}^p - G_i]) \]
for sample p, where n is the number of conditions, \( m_i \) is the mass, \( C_{m_i}^p \) is the VOC concentration of sample p at mass \( m_i \) (normalised to TIC and transmission corrected), \( G_i \) is the chosen limit, \( \varepsilon_i = \pm 1 \) depending on the kind of condition (upper or lower limit) we impose, and \( \theta(x) \) is the step function \( \theta(x)=1 \) for \( x>0 \) and \( \theta(x)=0 \) for \( x<0 \). Our method contains 20 conditions for concentrations on eight masses, e.g., the conditions for mass 81 (see Fig. 2) are: \( K_1 = -30, \varepsilon_1 = -1, G_1 = 1*10^{-3} \) and \( K_2 = +41, \varepsilon_2 = 1, G_2 = 7*10^{-3} \).

Fig. 2: Concentrations (normalised to the total ion signal (TIC) and transmission corrected) averaged over the groups 1-4, respectively, plus standard deviation, maximum and minimum value against group number. The ‘bad’ quality samples form the group 1, the ‘good’ quality samples the groups 2 – 4 (‘okay’, ‘good’ and ‘very good’).

If the CV of a batch has a positive sign the quality is ‘good’, if the CV is negative the quality is ‘bad’. Fig. 3 shows the CVs of all investigated samples (the quality value is related to the customer’s sensory description, quality<50 is ‘bad’, quality>50 is ‘good’). Our method allows to determine the consumer’s acceptability (‘good’/’bad’).

Furthermore, we successfully used this promising method for investigating the production process where we took samples at regular intervals during the process. With our method we were able to “watch” how the quality developed: some concentrations increased during the production
(see Fig. 4) whereas some decreased; the CV was negative at the beginning, increased and reached a positive value at the end of the production process. The goal of this study was to evaluate the ability of this method for controlling the production process.

Fig. 3: Condition value (CV) against quality (value related to the customer’s sensory analysis, ‘good’ quality > 50, ‘bad’ quality < 50). The CV is based on the PTR-MS data. CV < 0 means ‘bad’ quality and CV > 0 ‘good’ quality. We get a perfect agreement between our results and the customer’s sensory test.

Fig. 4: Normalised and transmission corrected concentrations of mass 89 and 97 averaged over three batches plus standard deviation, minimum and maximum value as a function of the production step.

**Acknowledgement**

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Comparison of the emission of volatile organic compounds from two strawberries clones by PTR-MS

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ABSTRACT

Aiming at the possible application of PTRMS to evaluate the different varieties of strawberries we carried out a study on two strawberry clones (Fragaria x ananassa). One (called MISS) is a commercial variety, the other is her “daughter” which is at the moment under evaluation. We discuss here the measured differences in emitted volatile organic compounds between the two genotypes for fresh fruits and during postharvest aging: the two clones are always clearly different from each other indicating that the two can be distinguished on the basis of their emitted VOCs. Moreover measurements at the harvesting day and on the successive 12 days give information on fruit stability and flavour changes both for room temperature storage (only 4 days) and 4°C storage. Time evolution of a few selected masses from the PTR-MD spectra is reported.

1. Introduction

Since childhood strawberry flavour is one of the most recognised and appreciated but a chemical definition of all the related compounds and of their relative ratios is still an open question [1]. This complex flavour mix is of extreme importance for leading consumer preference and its importance for variety selection cannot be overemphasised.

Up to now more than 400 volatile organic compounds have been detected in strawberries [2] and among the several chemical groups, esters seem to play a most important role. Beside the phenotypic volatile emission several other compounds can be found as a consequence of internal or external gene activation: senescence, parasite damage, other stress, etc., and they can strongly change the typical fruit aroma.

For this reasons it is important to follow shelf-life evolution of different varieties to understand flavour changes and, possibly, their relation with sensory analysis [3]. Due to its easy and fast application, PTRMS can probably be an useful tool for assessment of aroma pattern and its evolution during storage even in the very first steps of variety evaluation and selection. Previous works [4] indicated that PTRMS can effectively follow time evolution of volatile compounds emitted by berry-fruits during storage. Here we concentrate on the possibility of evaluating if there are differences between cultivars and how these differences change in time. Moreover reported data are obtained on single fruits and this is important to understand the real data spread and significance.

2. Materials and methods

We used a commercial PTRMS instrument [5] in standard configuration (Ionicon Analytik GsmbH). The stainless steel needle used for sampling was directly connected with the
reaction chamber (drift tube) by a 1/8” PTFE tube heated at 70°C. After staying at room temperature for two hours one fruit was put for 1 hour in a glass vessel (400 ml) provided with two PTFE/silicone septa on opposite sides. The inlet of the PTRMS was then connected with the vessel and a flux of 9.3±0.1 sccm was continuously extracted for 4 minutes (corresponding to the acquisition of 5 complete spectra); the missing air in the vessel was continuously replaced by lab air. To avoid possible systematic memory effects from one measurement to the next measurement the order of repeat measurements was changed and the apparatus was flushed with air for 15 minutes between the measurements. We also used different vessels for every fruit. We consider here spectra from a mass/charge ratio of 29 up to 260 converted in ppb as discussed in [5]. We stress that all presented measurements are obtained from single, intact, strawberry fruits without any treatment but the equilibration of the headspace at room temperature.

Presented data are part of a work started in spring 2002 on two strawberry clones under evaluation by ISF (Forlì, CS, Italy): MISS, a commercial variety, and her daughter called SEL.

Fig. 1: Spectra of MISS (lower panel) and SEL (upper panel) few hours after harvesting. Data are averages of 5 measurements on single fruits. Only the positive parts of the error bars (standard deviation) and the range from m/z=30 up to m/z=104 are displayed.

Fig. 2: Postharvest evolution of the total volatile compounds emission of MISS and SEL. Data for 1st and 4th day are average of 5 measurements on single fruits, the other ones are average of 3 measurements. Upper panel shows data for fruits stored at 4°C, lower panel for fruits at room temp.
On 29th April 2002 strawberry samples harvested in an experimental field in Verona (Italy) have been brought to our lab and partly stored at room temperature (16°C) and partly in a standard refrigerator at 4°C. After 4 days the fruits stored at room temperature showed evidence of drying followed by mould formation and we did not measure these samples any further. The other fruits (4°C) seemed to keep a good appearance for a longer time and have been measured for 12 days. On the 1st and 4th day we measured 5 fruits for each clone, on the other days 3 fruits.

3. Results and discussion

Fig. 1 shows a comparison between the PTRMS spectra of the two clones (average and standard deviation of 5 measurements on the harvesting day). Even taking into account the high error bars (note that the logarithmic scale reduces the apparent error bar) the clones are clearly different: SEL is in general characterised by a smaller intensities except for 19 masses (e.g. 59). On the contrary MISS has higher emission on several masses in particular on the series of masses that are mostly related with esters: 131, 117, 103, etc. However we noticed that, due to the high error, simple comparison of single mass intensity cannot unambiguously identify varieties.

Time evolution of total volatile emission detected by PTRMS is shown in fig. 2 for both, room temperature (shelf-life 4 days, lower panel) and 4°C storage temperature (12 days, upper panel). At room temperature fruits do not show clear variation of the total emission up to the 4th day where a clear increase, more evident for MISS, is observed. The high standard deviation of the measurements of the first day is not just noise but seems to be always present in our measurements. We suppose that this is due to postharvest stress conditions that are somehow smoothed during storage (see also, e.g., mass 45 and 47 for MISS in fig.3). For storage at 4°C we notice a clear difference in total volatile emission: MISS has always higher emission and a higher error bar. Being the number of samples the same for the two data sets these last aspects
indicate that SEL is a variety with less variability between different fruits and this can be an important commercial feature.

Some of the masses in PTRMS spectra can often be assigned, at least to a high percentage, to chemicals being important products in metabolic and catabolic processes: e.g. methanol (mass 33), ethanol (mass 47) and acetaldehyde (mass 45). In Fig. 2 post harvest time evolution of these masses is shown. Because every data point refers to a different fruit, shelf-life evolution is characterised also by an increase of the error (different fruits have different time evolution). Because of this in future studies it is probably better to follow the evolution of the same fruit as a function of time. Mass 33 (methanol) for MISS ranges between 2 ppm and 4 ppm showing an increase on the 4th day at room temperature. SEL has higher methanol values (4-8 ppm) and shows a similar evolution in time. For room temperature measurements the relative increase is more evident. Time evolution of mass 47 (ethanol, fig. 3 lowest panel) at room temperature shows a clear drop on the second day for MISS and the increase at the 3rd-4th day is clearer for SEL. Fruits stored at 4°C show a different behaviour: roughly constant for SEL, with a step from 70ppb to 90 ppb for MISS. Acetaldehyde (Mass 4, fig. 3 middle panel) seems to be a fast indicator of senescence because its increase is evident on the 3rd day for both varieties, one day before methanol and ethanol but it is also affected by a high variance between different fruits. Moreover also refrigerated fruits have a quite different behaviour: constant below 500 ppb for SEL with very weak time dependence, above 1000 ppm with a probable maximum/increase in the last days for MISS. Several other masses show interesting behaviour but will be discussed elsewhere.

4. Conclusions

Our measurements show that PTRMS can easily measure single strawberry fruits without any treatment and that the two considered clones are distinguished even in presence of the high observed variance (both from the measuring process and from the actual differences among fruits). One variety was the “daughter” of the other and this confirms that in the selection process the effect on flavour can be very strong. In this sense we propose that PTRMS can be an useful tool for breeders and scientists because it allows a fast and accurate qualification of the clones to be selected. Information on similarities with well established varieties and on shelf-life stability can be obtained practically “in field” and lead the selection process. Further studies on fragmentation of pure standards are however necessary to better understand the data and correlate them with physiological processes.

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References

Proton Transfer Reaction Ion Trap Mass Spectrometry (PTR-ITMS)

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We will present recent work at PNNL in collaboration with Ionicon involving the interfacing of the PTR-MS drift tube with an ion trap mass spectrometer (ITMS). This has been the subject of much speculation and discussion in the PTR-MS community. ITMS is appealing because of the ability to perform MS-MS and possibly distinguish between isomers and other isobars. There are, however, some serious questions, especially about the efficiency of injection of ions from the PTR-MS into the ion trap and the possibility of fragmentation upon injection into the relatively high ($10^{-4}$ Torr) pressure of the ITMS. We have constructed a prototype instrument using an Ionicon drift tube and a Finnegan Saturn ITMS. A schematic is shown in figure 1. The interface is designed to replace the standard electron gun and uses a simple einzel lens focus the ions from the drift tube exit into the ITMS. The goal here was not to achieve the ultimate sensitivity, but to determine the efficiency of ion injection and to understand how to improve sensitivity in a second-generation instrument. We will also present some examples of MS-MS spectra. The design for an improved PTR-ITMS will be discussed.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Schematic of PTR-ITMS showing drift tube, interface and ITMS}
\end{figure}
On-line monitoring of VOCs at a high mountain site in the German Alps

(Schneefernerhaus, Zugspitze)

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In the frame of the Schneefernerhaus Aerosol & Reactive Nitrogen Experiment (SCAVEX) a Proton-Transfer-Reaction Mass Spectrometer [Lindinger et al., 1998] has been installed on the Environmental Research Station Schneefernerhaus (47.42 N, 10.99 E, 2650 m a.s.l.). The Schneefernerhaus is situated about 300 m below the peak of the Zugspitze in the German Alps. PTR-MS measurements on high mountain sites can be used to identify air masses with very different chemical characteristics, which have originated in the planetary boundary layer or have undergone long-range transport in the free troposphere [Karl et al., 2001a,b, 2003]. From October 28, 2002 till this day the remotely operated PTR-MS instrument has been measuring a series of volatile organic compounds (VOCs) including oxygenates (methanol, acetaldehyde, acetone, methyl ethyl ketone), aromatics (benzene, toluene, alkyl substituted benzenes) and the biomass burning tracer acetonitrile. At this early stage of data evaluation we have focused on the observed [toluene]/[benzene] ratio which can be used to determine the photochemical age of anthropogenic impacted air masses. By assuming that both toluene and benzene are mainly removed by OH radicals, the [toluene]/[benzene] ratio in air changes as a function of time due to the different reaction rate coefficients of benzene and toluene with OH radicals with $k_{\text{toluene}+\text{OH}}/k_{\text{benzene}+\text{OH}} = 5.7$ [Atkinson et al., 1997]. Volz-Thomas and Kolahgar [2000] reported an initial [toluene]/[benzene] ratio of 2.0 for Europe. Fig. 1 shows the time evolution of toluene and benzene volume mixing ratios as observed on the Schneefernerhaus on December 18 and December 19, 2002. Fig. 2 shows the corresponding [toluene]/[benzene] ratio. A maximum [toluene]/[benzene] ratio of 1.3 was found at noon on December 18 implying a photochemical age of these air masses of only a few days. The spikes before midday and in the afternoon of December 18 are attributed to local emissions from the Schneefernerhaus or the adjacent ski resort. On the morning of December 19 a minimum [toluene]/[benzene] ratio of ~0.3 was observed. A photochemical age of these air masses of more than 2 weeks can be estimated.
Fig. 1: Time evolution of toluene and benzene volume mixing ratios (VMR) as observed on the Schneefernerhaus on December 18 and December 19, 2002

Fig. 2: [Toluene]/[Benzene] ratio as observed on December 18 and December 19, 2002

Back trajectory analysis provided by NOAA-CMDL is available to complement our data. The back trajectory arriving at the Zugspitze at noon on December 18 is shown in Fig. 3. Air masses originate in the boundary layer of Southwest Europe 7 days prior detection, move northward to Southern England at low altitudes and start ascending 3-4 days prior to arrival at the Schneefernerhaus. Back trajectory analysis confirms our finding that air masses which were sampled on December 18 had been anthropogenic impacted about 4-5 days prior to arrival at the
Schneefernerhaus site. The back trajectory arriving at the Zugspitze at noon on December 19 is shown in Fig. 4. Air masses originate in North America at altitudes > 1 km and cross the Northern Atlantic Ocean in about one week. Again back trajectory analysis confirms our finding that on December 19 photochemically aged air which had not been anthropogenically impacted for more than a week was sampled.

Fig. 3: Back trajectory arriving at the Schneefernerhaus on Dec. 18, 2002 12.00 UTC

As shown in Fig. 5 and 6 enhanced methanol and acetone volume mixing ratios of ~0.6 ppbV and ~0.8 ppbV respectively were observed on December 18 in European air masses. On December 19, when air masses from North America were encountered, methanol and acetone
volume mixing were still significantly enhanced being 0.5 ppbV and 0.6 ppbV, respectively. Methanol and acetone have both biogenic and anthropogenic sources \cite{Heikes2002, Jacob2002}, but, as mentioned above, these air masses had not been continentally impacted for more than a week. Since both methanol and acetone have an atmospheric lifetime of more than a week, long-range transport may be the reason of the observed methanol and acetone enrichment in free tropospheric air.

Fig. 5: Volume mixing ratios of methanol in the period 17.12.2002 - 21.12.2002

Fig. 6: Volume mixing ratios of acetone in the period 17.12.2002 - 21.12.2002

References


Validation of Atmospheric VOC Measurements by Proton-Transfer-Reaction Mass Spectrometry using a Gas-Chromatographic Pre-Separation Method

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Abstract
Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a useful tool to study volatile organic compounds (VOCs) in the atmosphere. In PTR-MS, proton-transfer reactions with H3O+ ions are used to ionize and measure VOCs in air with a high sensitivity and fast time response. Only the masses of the ionized VOCs and their fragments, if any, are determined, and these product ions are not unique indicators of VOC identities. Here, a combination of gas chromatography and PTR-MS (GC-PTR-MS) is used to validate the measurements by PTR-MS of a number of common atmospheric VOCs. We have analyzed 75 VOCs contained in standard mixtures by GC-PTR-MS, which allowed detected masses to be unambiguously related to a specific compound. The calibration factors for PTR-MS and GC-PTR-MS were compared and showed that the loss of VOCs in the sample acquisition and GC system is small. GC-PTR-MS analyses of 56 air samples from an urban site were used to address the specificity of PTR-MS in complex air masses. It is demonstrated that the ions associated with methanol, acetonitrile, acetaldehyde, acetone, benzene, toluene and higher aromatic VOCs are free from significant interference. A quantitative inter-comparison between PTR-MS and GC-PTR-MS measurements of the aforementioned VOCs was performed and shows that they are accurately measured by PTR-MS.
Comparison of VOC measurements in Nashville, TN, during the Southern oxidants study (SOS) 1999

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During the Southern Oxidants Study (SOS) 1999 Nashville campaign ambient air samples were analyzed at Cornelia Fort Airport (CFA) for volatile organic compounds (VOCs) by two independent methods:

1. a gas chromatographic system (AL, NOAA) [Stroud et al., 2002], which collected and analyzed air samples for VOCs every 60 minutes

2. a proton transfer reaction mass spectrometer (Univ. of Innsbruck) [Lindinger et al., 1998] which measured a series of VOCs on a time shared basis for 5 to 15 seconds respectively, once every 5 minutes

Good agreement was obtained for acetaldehyde, isoprene, the sum of methyl vinyl ketone (MVK) and methacrolein (MACR), the sum of acetone and propanal and the sum of methyl ethyl ketone (MEK) and butanal. The PTR-MS system is not able to distinguish between isobaric compounds implying that for such species sum values have to be reported. For the compounds mentioned above good agreement between the two methods was achieved.

![Acetone and Propanal](image)

Fig. 1. Synoptic variations for acetone and propanal for the time period June 18 to June 28 as observed at Cornelia Fort Airport in Nashville, TN, during SOS 99. Triangles represent in-situ PTR-MS results, dots: NOAA's GC measurements.
Fig. 2. Scatter plots of coincident PTR-MS and GC measurements for acetone and propanal for the time period June 18 – June 28 obtained during SOS 99 in Nashville, TE.

References


An Intercomparison of Airborne VOC and PAN Measurements

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As part of the Texas Air Quality Study (TexAQS 2000) an informal airborne intercomparison has been conducted to evaluate the state-of-the art of fast-response, in-situ methods for analyzing Volatile Organic Compounds (VOCs) and peroxyacetyl nitrate (PAN). Instrumentation included a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS), the Tropospheric Airborne Chromatograph for Oxy-hydrocarbons and Hydrocarbons (TACOH) and a gas chromatograph for PAN detection using electron capture detection (GC/ECD). The measurements were made in the Greater Houston area and East Texas in August/September 2000 during 13 flights with the NSF/NCAR ELECTRA aircraft. The intercomparison was conducted mainly in the boundary layer but included some encounters with air masses from the free troposphere. The sample protocols were quite different for the different methods. The GC/ECD instrument and TACOH system collected and analyzed air samples every 3.5 and 15 minutes, respectively. The PTR-MS system sequentially measured a variable number of compounds (2-10 seconds integration time per compound) once every 4-40 seconds depending upon the number of measured compounds. PTR-MS data measured within the GC sample acquisition period ± 10 seconds were used for the intercomparison. Final results from the intercomparison show that measurements of acetaldehyde, isoprene, the sum\textsuperscript{*} of acetone and propanal (*PTR-MS does not distinguish between isobaric species), the sum\textsuperscript{*} of methyl vinyl ketone and methacrolein and toluene agree reasonably well. Poor agreement was achieved in the case of methanol and the underlying sensitivity problem in the PTR-MS or the TACOH system is under investigation. The results of the PAN intercomparison indicate that the PTR-MS technique suffered from an interference most likely associated with the presence of peracetic acid in photochemically aged air. When this interfering signal was traced by periodically inserting a selective PAN scrubber (thermal decomposition) into the sample air stream and subtracted from the original signal, the PTR-MS PAN data were in very good agreement with the GC/ECD results.
Absolute Quantification of Headspace Volatiles by PTR-MS

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ABSTRACT
One of the outstanding properties of PTR-MS is that it allows for a direct and absolute quantification of volatile organic compounds in the gas-phase. Here we examine this on a model sample of known concentration. The headspace of an ethyl butyrate solution is stripped for 14 hours with a flow of 500 sccm/min, until the solution is completely depleted from ethyl butyrate. The measured PTR-MS count-rate is transformed into \( \mu \text{g/min} \) of released ethyl butyrate. The cumulated amount turns out to be within a few percent of the initial 1000 \( \mu \text{g} \) present in the solution. We then apply the method to in-mouth aroma release of ethyl butyrate, to quantify breath-by-breath the quantity exhaled through the nose. Currently, several experimental parameters that are not fully taken into consideration may affect a direct quantification (e.g. transmission function of MS, humidity of sample gas). Work is underway to resolve these issues.

1. Introduction
Absolute quantification of volatile organic compounds (VOC) in the headspace (HS) of food products are rarely reported in the literature, although it is generally agreed that the HS is relevant to the aroma that a consumer perceives. E.g. on coffee, essentially all quantification of VOCs was performed on liquid (brew or instant) or roast and ground coffee (1). Furthermore, methods applied in aroma research for VOC quantification are tedious and time consuming (2). In this context, it is remarkable that an often cited characteristic of PTR-MS is the fact that measured count rates (cps) of individual VOCs can be directly transformed into absolute HS concentrations. This feature has been discussed in a series of papers (3,4). Here we re-visit and discuss fundamental conditions of this particular and crucial aspect of the method, and add a quantitative verification. Currently, work is underway to examine in more details the precision and statistic of HS quantification via PTR-MS.

2. Absolute Concentrations of VOC in the Gasphase [ppb,]
As outlined in references (3,4), a simple relation exists between experimentally measured PTR-MS mass spectral intensities (in unit of cps) and the actual HS density (Equation 1).

\[
[RH^+\text{]} = [\text{H}_3\text{O}^+] \cdot (1 - e^{-k[RH^+\text{]} t}) = [\text{H}_3\text{O}^+] [R] kt
\]  

(1)

The HS density of VOCs, [R], is proportional to the ratio between measured count rates of the protonated VOCs, [RH\textsuperscript{+}], and the primary ion signal, [H\textsubscript{3}O\textsuperscript{+}], and inversely proportional to the reaction rate constant \( k \approx 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \), and the reaction time \( t \approx 105 \text{ ms} \). For practical purposes, a more explicit formulation is required, that takes account of the specific physical conditions in the reaction chamber (drift-tube) and of the mass separation in the quadrupole mass filter. Hence, Equation 2 gives a more explicit and practical formulation of the situation.

\[
(RH^+\text{]}\text{[ppb]} = \frac{[RH^+\text{]}_{\text{counts}} \cdot 1.013 \cdot 22400 \cdot \left(273,15 + T_d\right) \cdot T_{H_3O^+}}{k \cdot t \cdot [H_3O^+]_{\text{counts}} \cdot P_d \cdot 6.022E23 \cdot 273,15 \cdot T_{RH^+}}
\]  

(2)

\( [RH^+\text{]}\text{[ppb]} \) = Concentration of VOC in units of part per billion in the gas phase
\( [RH^+\text{]}\text{[counts]} \) = Counts-per-seconds of ion mass corresponding to compound VOC
\( [H_3O^+]\text{[counts]} \) = Counts-per-seconds of the primary ion \( H_3O^+ \)
\( T_{H_3O^+} \) = Transmission of quadrupole MS at the mass of the primary ion \( H_3O^+ \)
\( T_{RH^+} \) = Transmission of quadrupole MS at mass of VOC
\[ P_d \] = Pressure in drift tube in units of bar
\[ T_d \text{[°C]} \] = Temperature in drift-tube
\[ k \] = Reaction rate constant [cm\(^3\)/s]
\[ t \] = Reaction time

Several comments need to be made at this point.

**Reaction rate, \( k \):** Measurements of reaction rates for a large range of VOCs has revealed that the experimental values for VOCs of interest to food aroma are very close to \(2 \times 10^{-9}\) cm\(^3\)/s (within a few percent). Therefore this average values is often used as an approximation for all VOCs. Any improvement beyond this approximation requires that one specifically measures the reaction rate of the VOC under study (in case it is not already reported in the literature).

**Reaction time, \( t \):** The reaction time is the time available to neutral VOCs to be ionised by proton transfer from H\(_3\)O\(^+\), provided the proton affinity of the neutral is higher than of the primary H\(_3\)O\(^+\) ion (166 kcal/mol). It depends on the ion mobility in the drift-tube, which is influenced among others by the temperature and the composition of the buffer gas. E.g. the ion mobility may change by more than 20% at higher concentrations of water vapour in the buffer gas, relative to a dry buffer gas.

**Transmission function of the quadrupole MS:** As discussed in textbooks on quadrupole MS, transmission of ions may vary with mass and depends on the particular potentials on ion lenses and MS settings. It is therefore not possible to derive a universal transmission function. In our laboratory, we regularly measure the transmission function of our instruments and use this to correct the measured ion count rates. Yet, it remains that the transmission curve is based on transmission measurements at a few discrete masses, and should not be extrapolated outside the mass range of calibration.

**H\(_3\)O\(^+\) at counts:** Since the ratio between H\(_3\)\(^{16}\)O\(^+\) (m/z 19) and H\(_3\)\(^{18}\)O\(^+\) (m/z 21) is very close to 500, and no background is expected at m/z 21, it is more common to measure the primary ion signal using the count rates of m/z 21. Multiplying the measured count-rates at m/z 21 by 500, one obtains the ion density at m/z 19. This spares the secondary electron multiplier and prevents that the density of primary ion H\(_3\)O\(^+\) is underestimated due to saturation of the multiplier.

![Figure 1](image_url)

**Figure 1:** Conversion of cps to ppb\(_v\). The example shown is the reconstitution of 0.2 gram instant coffee with 100 ml water at room temperature. The coffee was not stirred. Considering that it took 8 s to add the 100 ml water to the instant powder, the burst of volatiles observed upon reconstitution was essentially instantaneous.

3. Absolute Quantities of VOC in the Gasphase [\(\mu g\)]
In order to verify, for our apparatus, the validity and precision of Equation 2, we prepared 100 ml of a solution containing 10 mg/L of ethyl butyrate. This corresponds to a total of 1000 µg ethyl butyrate. The solution was placed in a closed 120 ml glass cell and purged for 14 hours at 500 standard cubic centimetre (sccm) per minute. This led to a gradual depletion of the solution. Figure 2 shows the concentration of ethyl butyrate, where the vertical axis is expressed in µg.

![Figure 2: Cumulative release of 1 mg ethyl butyrate from a stripped HS cell, as quantified with PTR-MS. The trace for the release quantity per cycles (circles) is magnified by a factor of 200, in order to plot it on an identical vertical axis with the cumulated quantity.](image)

A unit-transformation in Equation 2 allows converting ppb, to µg as shown in Equation 3.

\[
C_{(VOC)} = \frac{M_{(VOC)} \cdot F \cdot P_{atm} \cdot cps_{(VOC)}}{cps_{(19)} \cdot N \cdot k \cdot t \cdot P_{drift}}
\]

- \(C_{(VOC)}\) [g/min] = quantity of VOC released per minute
- \(M_{(VOC)}\) [g/mol] = molecular mass of VOC
- \(F\) [sccm] = flow rate in standard cubic centimetre per minute, taking into account the purge, the dilution and the humidity
- \(P_{atm}\) [mbar] = atmospheric pressure
- \(cps_{(VOC)}\) = PTR signal intensity of VOC
- \(cps_{(19)}\) = PTR signal intensity of primary ion H_3O^+
- \(N\) [mol\(^{-1}\)] = Avogadro’s number 6.0220*10\(^{-23}\) mol\(^{-1}\)
- \(k\) [cm\(^3\)/s] = rate coefficient = 2*10\(^{-9}\) cm\(^3\)/s
- \(t\) [s] = reaction time = 105*10\(^{-6}\) s
- \(P_{drift}\) [mbar] = Drift tube pressure

Stripping an ethyl butyrate solution containing a total amount of 1000 µg with a flow of 500 sccm per minute during 14 hours, the volatile ethyl butyrate is gradually stripped from the solution. The time vs. µg/min trace (circle) in Figure 2 reflects this depletion over time. The amount of ethyl butyrate released during stripping gradually decreases until all is removed from the solution. The second trace in Figure 2 (full line) shows the cumulated quantity of ethyl butyrate released during stripping. (In order to plot both traces on the same vertical axis, the time vs. µg trace was multiplied by a factor of 200). The cumulated quantity of released ethyl butyrate initially increases rapidly and reached after about 8 hours a value very close to the 1000 µg. While this quantification yields a value only a few percent off the actual one, more trials are needed to assess the precision of the quantification by PTR-MS.

In spite of the high accuracy of the above reported value, it is important to mention that several potential sources of errors in the absolute quantification of VOCs by PTR-MS remains. (i) Flow-controllers may not be precisely calibrated. For this work, flow-controllers were checked just prior to measurements. ii) Often only the approximate value of 2*10\(^{-9}\) cm\(^3\)/s for the reaction rates of VOCs are used. In some cases this may be off by 20% of the real value, although for a large number of VOC the error is much smaller. (iii) The transmission function is often measured on just a few masses, and interpolated to the complete mass range. This may introduce errors of more than 5%. Here, we have used ethyl butyrate, whose mass is m/z 117. In this mass range the transmission function of our quadrupole MS goes through a smooth plateau with a transmission
very close to 1. Furthermore the transmission at m/z 21 is measured very precisely. (iv) Ion mobility may change due to changes in the composition of the buffer gas (mainly due to changes in humidity). This affects the reaction time, \( t \). (v) At higher levels of humidity in the sample gas, cluster formation between VOCs and \( \text{H}_2\text{O} \), and in particular formation of \( (\text{H}_2\text{O}\cdot\text{H}_3\text{O})^+ \), may become important, inducing switching reaction. This changes the reaction conditions inside the drift tube. (vi) A too high concentration of \( \text{O}_2 \) in the source may generate chemical ionisation reactions with the primary reaction ion \( \text{O}_2^+ \). This will change the conditions for chemical reaction in the drift tube. All these points have to be considered, if on-line analysis by PTR-MS shall become a precise tool for the quantification of HS volatiles.

4. Quantification of In-Mouth Release

In-vivo (or sometimes also termed nosepace or in-mouth) aroma research is a relatively young field. It is born from the idea that what most matter to a food consumer is the aroma that is released in mouth during drinking or eating. Aroma perception during food consumption is related to VOCs that reach the olfactory epithelium in the nose. This aroma transported from the oral cavity via the pharynx to the nasal cavity is called the retronasal aroma. One approach to analytically explore this dynamic aroma is via on-line nosepace analysis (5-7).

In Figure 3 we show the breath-by-breath release of ethyl butyrate while eating ice cream. One trace shows the temporal profile of the ethyl butyrate exhaled through the nose, oscillating with the breathing rhythm of the assessor. The vertical axis is expressed in \( \mu\text{g} \) exhaled volatile. The second trace gives the cumulated quantity of the VOC. Such a quantitative presentation of nosepace data may allow to better asses the sensory significance of measured intensities.

5. References

Coupling GC-MS with PTR-MS for Unambiguous Chemical Characterisation of On-Line PTR-MS Spectra

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ABSTRACT
This paper introduces a significant technical extension of Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS). Coupling gas-chromatographic (GC) neutral separation to simultaneous detection by PTR-MS and Electron-Impact-MS, an ambiguous chemical interpretation of complex PTR-MS spectra becomes feasible. In order to exploit the full potential of the coupling, the PTR-MS was upgraded with the recently introduced Fast Drift Tube (FDT). Here a detailed discussion of selected technical aspects, necessary to operate the novel set-up under controlled and stable conditions, will be given. We will focus in particular on critical modifications of the PTR-MS, the GC EI-MS and the automatic thermal desorber (ATD)

1. Introduction
Since the first publication on PTR-MS in 1993 by W. Lindinger and co-workers [1], the technique has been steadily improved and the range of applications extended [2-8]. Today, PTR-MS is an established technique providing novel and often unexpected findings in a variety of fields. Monitoring complex mixture of volatile organic compounds (VOC) on-line with a high time resolution is one of the most significant characteristics of PTR-MS. Depending on the concentration of the VOCs and the number of ions being monitored simultaneously, a sub-second time resolution may be accomplished. Yet, in order to assign PTR-MS ion peaks to chemical compounds, two important issues have first to be addressed [2].

First: PTR-MS is a one-dimensional method that characterises compounds by their mass. Relative to GC analysis, which separates along the convoluted and complex axis of retention times, mass is an intrinsic and stable property of molecules. Hence separation by mass rather than retention times seems to allow a more straightforward identification of compounds. Yet, except in a few simple systems, real foods are characterised by a large number of volatile organic compounds (VOC), where some have the same mass (isobaric). Hence, mass-information alone is often insufficient for unambiguous identification. A similar problem is encountered in GC. Retention times alone are generally not sufficient for identification and therefore GC is often coupled to MS or other additional detectors to achieve a multidimensional characterisation.

Second: PTR-MS suffers from some ionisation-induced fragmentation which may complicate the interpretation of spectra. While about 80% (in coffee) of the mass spectral intensity appear at parent masses [2], it is nonetheless important to consider fragmentation for proper assignment. Both the one-dimensionality of the method and the ionisation-induced fragmentation make a direct identification of HS compounds, based solely on PTR-MS spectra, questionable. In order to address this limitation, a series of approached were discussed in the literature [2]. Yet, the one-dimensionality has remained a crucial drawback. Here we present an approach which allows to remove to a large extend the ambiguity in the identification of chemical compounds in on-line PTR-MS spectra. A more complete discussion, together with applications will be provided in a forthcoming publication [C. Lindinger, P. Pollien, S. Ali, C. Yeretzian; in preparation].

2. Experimental: Combining GC, EI-MS and PTR-MS
For an unambiguous chemical characterisation of dynamic PTR-MS spectra, we propose here to take a two step experimental approach.
First Step: In PTR-MS experiments, approximately 14 sccm/min of sample gas is continuously introduced into the PTR-MS. But, in essentially all PTR-MS experiments, the available flow of sample gas is significantly higher that 14 sccm/min. This is either because gas flows are intrinsically high (e.g. coffee roasting, or nose-space analysis), because volatile concentrations are too high and the sample gas has to be diluted to avoid saturation of the MS detector (e.g. above-the-cup aroma release from coffee) or because the humidity is too high for proper operation of the drift tube (e.g. headspace analysis from hot liquids; > 50°C). Hence most of the sample gas bypasses the PTR-MS and is released either into the laboratory air or a gas-exhaust line. Instead of discarding this excess gas flow, here we introduce a tenax trap into the gas exhaust line of the bypass. Adsorption on the trap during a few minutes is often sufficient for subsequent analysis (see below). If necessary, a series of tenax traps can be used to trap gas at different times of the experiment. The question now resides in linking the compositions of the trapped VOCs to the corresponding PTR-MS spectra.

Second Step: The classical approach for unambiguous identification of volatile aroma compounds in flavour research consists of GC separation with EI-MS detection. Identification of GC-separated, electron-impact (EI) ionised, and mass-separated ion distributions is achieved via sophisticated matching algorithms using large databases of EI spectra. In our case we not only need to characterise the trapped gas, we also have to link this to the corresponding PTR-MS. In order to provide a practical solution to the problem outlined above, we have opted for a solution, which combines PTR-MS as detector to GC EI-MS. In essence, it consists in an initial GC separation. The GC effluent is split in two portions and injected simultaneously into a conventional EI-MS and a PTR-MS respectively. A constraint that we set was that the PTR-MS on the one hand and the EI-MS on the other hand should remain fully operational as individual and independently instruments. A schematic of the final set-up is show in Figure 1. The set-up was separated in its three main components (modules) consisting of the ATD (for thermal desorption of tenax traps), the PTR-MS and the GC EI-MS. Each module was individually adapted with respect to the physical dimensions of the tubings (mostly passivated fused silica), equipped with additional flow and temperature controls and made compatible with respect to the carrier gases used. In the following a brief description of the set-up will be given.

ATD (automatic thermal desorber): The gas adsorbed on the tenax trap is desorbed on the ATD (Perkin Elmer; ATD 400) and swept with a flow of helium onto the GC column (column 1 in Figure 1). In standard instruments, the carrier gas flow (He) supplied by the ATD is pressure controlled. In order to connect the ATD to the GC EI-MS and PTR-MS, it has to be modified such as the flow rather than pressure is controlled. This was a necessary condition in order to have well defined gas flow conditions at the split to EI-MS and PTR-MS at the end of the GC column 1.

In addition to the injection port for the ATD, the GC was equipped with a standard split/splitless injection port to a second column (column 2; 30 m long, 0.53mm inner diameter). An auto sampler permits samples to be cooled or heated and shaken prior to injection. It is used either for liquid injection by a syringe or gas injection from SPME fibres. One important function of this second injection port is to determine accurately fragmentation pattern of compounds in PTR-MS. Commercial pure compounds may contain either traces of impurities, solvents or are partially degraded during storage. GC separation prior to introduction into the PTR-MS allows to unambiguously relate a PTR-MS ion distribution to chemical compounds. Valve #1 (Valco 4N4WT 350°C), mounted inside the GC oven switches between the two injection ports and the corresponding GC columns, and connects the GC effluent gas either to the glass split towards the detector section or alternatively to the exhaust line (column-exhaust).

PTR-MS: The inlet system of a commercial PTR-MS was modified to allow the effluent from a GC to be injected into the PTR-MS. In addition to the existing two inlets (online inlets, Figure 1) a third inlet to the PTR-MS was needed. Several technical issues had to be resolved in this context, some of which we will shortly outline here.
The coupling between the GC output and the PTR-MS input was accomplished via a 2 meter long passivated fused silica tubing of 0.53 mm inner diameter (L2) and two 4-port valves (valves #2 and #3). The tubings can be heated up to 150°C ($\vartheta$5). This allows for a very accurate control of pressures and gas flows from the GC to the PTR-MS. To minimise losses of time resolution due to the gas transfer from GC to PTR-MS, dead volumes in connections and valves were minimised and lines were passivated (Si-coating). One critical element for stable operations of the coupling was a pressure controlled bypass system (PC and membrane pump). This was necessary to guarantee defined pressure conditions in the drift tube of the PTR-MS.

An additional problem to be resolved was the incompatibility of carrier gas between GC and PTR-MS. GC EI-MS works with He carrier gas at $1 \times 10^{-4}$ - $1 \times 10^{-5}$ mbar while the drift tube of the PTR-MS needs Air or N$_2$ as buffer gas at 2.0 mbar. To allow a proper coupling of GC with PTR-MS, the effluent gas from the GC column is mixed with a tenfold volume of N$_2$ gas (or alternatively with air). This dilution assures that the ion mobility in the drift tube is not significantly affected by the residual He content of the buffer gas. A flow controller (FC2) controls admixture of N$_2$ to the He carrier gas. To avoid back-diffusions of N$_2$ to the EI-MS, a 1m capillary line is introduced between the split and the N$_2$ admixture (deactivated fused silica tubing with 0.25 mm inner diameter). The dimensions of the capillary were chosen such as a stable flow of 1.5 sccm/min is maintained at the split to the PTR-MS. For GC column carrier gas flows in the range 2 to 4 sccm/min, this specific set-up guarantees that defined flow conditions can be maintained in the mixing region (admixture of N$_2$).

Since a PTR-MS mass-scan over a 200-amu mass range takes about one second, special attention was paid in choosing a column adapted to our needs. Column 1 is a 60 meter long column with an internal diameter of 0.53 mm and a thick coating film, resulting in a peak width of at least 4 seconds full width at half height. (Column 2 for liquid injection is 30 meter long with identical column diameter and coating). Choosing a GC carrier gas flow in the range of 2 to 4 sccm/min, the linear velocity (0.15 to 0.30 m/s) through the column results in a good separation of most of the molecules of interest to us.

**EI-MS:** The GC-oven and mass spectrometer are a combination of Finnigan Thermo Quest (Trace 2000 series) and an Automass Multi MS. The main modification relative to normal GC EI-MS operations is that a split is introduced at the effluent side of the GC column. GC EI-MS operates with He carrier gas, at $1 \times 10^{-4}$ - $1 \times 10^{-5}$ mbar. It is connected with a thin glass capillary to the GC column were the carrier gas flow control maintains vacuum in the EI ionisation chamber. In contrast, the drift tube of the PTR-MS operates with Air or N$_2$ as buffer gas at 2.0 mbar. The challenge was to maintain stable pressure and flow conditions for the whole set-up. In analogy to the PTR-MS side, a 1 meter long deactivated fused silica tubing of 0.1 mm inner diameter was introduced between the split and IE-MS input.

**3. Putting all Together:**

The final step is to combine the various informations to fully assign the intensities of each ion peak of a PTR-MS. The VOCs desorbed from the tenax trap correspond to the integrated volatile composition during a time window of a PTR-MS experiment. Once desorbed and separated by GC, the effluent is split into two parts and simultaneously injected into the two detectors: EI-MS and PTR-MS. GC EI-MS in combination with commercial databases on EI fragmentation allows in most cases to identify the compounds. In parallel the GC effluent is injected into the PTR-MS, revealing the PTR-MS ion distribution for the respective pure compound. Collecting this information for the whole GC chromatogram, it becomes feasible to precisely assign a PTR-MS profile. In case several compounds contribute to the same PTR-MS ion peak, one can determine the quantitative contributions of each compound. The novel set-up was successfully tested on a series of samples including complex examples such as the dynamic above-the-cup headspace of an espresso coffee. Applications will be reported separately.
Figure 1: Schematic of the GC – EI-MS and PTR-MS set-up for unambiguous chemical characterisation of PTR-MS ion peaks.

4. References
In-Vivo Analysis of Aroma Release while Eating Food: A Novel Set-up for Monitoring On-Line Nosespace Air

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ABSTRACT
An improved design for on-line analysis of in-mouth (in-vivo) aroma release while eating food and drinking beverages was developed at the Nestlé Research Center. It addresses two shortcomings of former set-ups. On the one hand, it permits sampling breath-air under conditions close to a natural eating situation. The ergonomic design of the nosepiece allows panellists to breathe freely and comfortably and to have some freedom of movement while performing the experiment. On the other hand, the novel sampling set-up achieves high sensitivity and time resolution of the analysed breath-air volatiles. Here we discuss technical aspects of the solution and demonstrate on two examples its performance. This includes release of aroma compound from liquid model systems, and in-mouth aroma release from a freshly prepared espresso coffee.

1. Introduction
The most important determinate whether a person will like a particular food product is its flavour. In a recent survey on the food buying and eating habits in the US, 96\% of the respondents said that taste outweighs all other factors \cite{1}. \textquotedblright{}Two-thirds said that healthy, nutritional food is very important to them when they shop. Asked to define healthy food, 58\% say \textit{fresh} and 44\% define it as \textit{low fat}. Such a consistent consumer attitude about the role of flavour in determining preferences and buying behaviour is the main driving force to the study of food flavour.

Progress in the field of food flavour research was marked by two major innovations. The first was the introduction of gas chromatography coupled to mass spectrometry. It strongly accelerated the identification of novel volatile compounds. Yet, it was soon recognised that only a small fraction of volatiles are odoriferous, and that it was important to differentiate between odour active and non-odoriferous volatiles. This was accomplished by the introduction of gas chromatography olfactometry methods in the mid 1980\'s, leading to a second acceleration in flavour research. Coupled with the increasing sensitivity of mass spectrometers, a large body of knowledge was assembled on the identification and quantification of many foods' odour-active compounds. Thus, on the flavour chemistry side, we know by now rather precisely which compounds are present above the odour threshold and can contribute to the overall flavour impression, for many of today\'s important food products.

In parallel to this effort in analytical flavour research, sensory analysis is often conducted on complex food products to evaluate an induced flavour profile change. However, the changes seen sensorially are sometimes difficult to explain by changes in flavour compound composition. Studies are needed to bridge this gap between flavour chemistry of single molecules and sensory perception of complex flavourings. Several fields work towards this goal as they study the relationships between compound concentration and perceived intensity, mixture perception, and compound synergy and suppression, among others. Nosespace analysis can aid in this understanding, as we can measure the actual compound concentration close to the olfactory receptors, as well as monitor its temporal evolution.

2. Experimental: Nosespace analysis
Aroma perception from foods during eating and drinking is related to volatile organic compounds that reach the olfactory epithelium in the the nose. During mouth movements
(mastication) and in particular swallowing, volatile compounds are transported from the oral cavity to the pharynx. The air flow of the subsequent exhalation sweeps the volatiles in the pharynx (and eventually aspires some air from the oral cavity) and releases it through the nose. During their transport from the pharynx through the nasal cavity, aroma compounds pass along the olfactory epithelium and may trigger a (retronasal) aroma perceptions.

The significance of retronasal aroma stems from the fact that it reflects the aroma perceived by consumers. One approach to analytically explore this dynamic aroma is via on-line nosespace analysis. Two related analytical techniques have proven particularly powerful in examining volatiles exhaled through the nose. These are Atmospheric Pressure Chemical Ionisation Mass-Spectrometry [2-4], and Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) [5-6].

Here we introduce a novel design of the nosespace experiment, developed at the Nestlé Research Center. It addresses two shortcomings of former designs, one related to the comform of the assessors during experimentation, and the other to improve the sensitivity and dynamic time-resolution of the breath-air sampling set-up. The solution we propose is illustrated Figure 1.

![Figure 1](image-url)

**Figure 1** Schematic of the nosepiece for sampling breath-by-breath the air exhaled through the nose during eating and drinking. Air exhaled through the nose is collected and combined into one larger tube of 7-mm inner diameter, which is open to the laboratory. A person with a regular breathing exhales approximately 4-5 litre of air per minute. In our experiments, the majority of the breath-air is released into the laboratory air. Only 80 ml/min of the breath-air is drawn up for analysis into a heated stainless steel tubing of 0.53 mm inner diameter. The tube is inactivated with inner quartz coating (“silcosteel®-tube from RESTEK, Bad Homburg, Germany). These 80 ml/min are split into two fractions: 14 ml/min is introduced into the drift tube of the PTR-MS, and the remainder is released through a pressure controller and membrane pump into the laboratory air. All tubings are heated to 70°C to prevent condensations.

We propose a novel ergonomic design of the nosepiece which allows panellists to breathe freely and comfortably. In particular, (i) panellists can breathe without feeling perturbed by the nosepiece; (ii) they have some freedom of movement of their head, and (iii) can eat and drink under conditions close to a natural eating situation. The air exhaled through the nose is sampled via two glass-tubings. Each panellist has an individual nosepiece, tailor-made in order to smoothly and comfortably fit into the nostrils. The nosepiece is fixed on laboratory eyeglasses, and connected to the PTR-MS via a flexible and heated tubing. The two tubings, sampling the breath-air, are curved upwards to leave free space in front of the mouth. Overall, this design allows panellists to perform experiments under conditions that mimic as close as possible a natural eating and drinking situation. (A detailed discussion will soon be published.)

PTR-MS is capable of monitoring the full breath-by-breath dynamic of a series of aroma compounds simultaneously and at high sensitivity. Technically, a time resolution of about 0.2 seconds can be achieved in our set-up [7]. In actual experiments, the time resolution is limited by the number of compounds that are simultaneously recorded and the respective concentrations in
the breath-air (which determines the required dwell-time in order to have a signal-to-noise ratio larger than three). In most practical situations, a time resolution of 1 seconds seems sufficient.

3. Results and Discussion

The novel set-up was applied to a series of samples including model systems and real food products. Here we present just two examples. The first example concerns a nosespace study using twelve different samples and five panellists. The samples were water, skim milk, 2.7% fat milk, and 3.8% fat milk spiked with five aroma compounds at three different concentrations. For a detailed discussion of this study, we refer to a forthcoming publication [D. Roberts, P. Pollien, N. Antille, C. Yeretzian; JAFc, submitted]. In short, the peak height of the first exhalation after swallowing a 10-ml sample was used as the nosespace value. A large interpersonal variability was observed where the female panellists released significantly less than the male panellists. Examining the intrapersonal variability, compounds with higher air-water partition coefficients showed the highest variability between panellists and the highest variability among replicates. The method had an average coefficient of variation of 33%. Furthermore, it was found that the percent released from the aqueous solution was less than 1%, while 99% of the aroma was swallowed without being released.

Figure 2. Example of nosespace analysis showing 5 replicates in series of liquid sample consumption, with 2 minutes breathing between each sample (only three of the five compounds are shown here – besides the \((H_2O\cdot H_3O)^+\) signal at m/z 37). This example was with skim milk, at the moderate flavour concentrations showing release of aroma compounds and the water cluster. \((H_2O\cdot H_3O)^+\) forms from the addition of the \(H_3O^+\) to water that is naturally present in the breath. In these experiments, we have opted for a time resolution of 0.5 sec, corresponding to 100 ms dwell time per compound.

The second example concerns the breath-by-breath analysis of a freshly prepared espresso coffee. Here again, we would like to refer to a forthcoming publication for a more detailed discussion [P. Pollien, C. Lindinger, S. Ali, C. Yeretzian; in preparation]. Briefly, We investigated the retronasal aroma profile while drinking an espresso coffee, and compared this to the orthonasal profile as sniffed above a cup. While both aroma profiles are dynamic and evolve with time, the retronasal aroma shows changes at a much shorter time scale and has various characteristics specific to the in-mouth situation. First, we observe a very rapid decrease of retronals volatile intensity and a concomitant change in volatile profile, indicating that the aroma of coffee evolves in the mouth. Second, a distinct volatile profile appears, with respect to intensity and volatile distribution, in the first exhalation after coffee is swallowed ("swallow-peak"). Finally, some volatiles persist in the breath-air after swallowing, fading only
slowly with time (afterodor). All these dynamic phenomena reflect the aroma of coffee as it is released in the mouth.

**Figure 3.** Nosespace profiles of four selected compounds during drinking of coffee. These four compounds were selected to document various dynamic in-mouth aroma release phenomena, while a total of 22 compounds were monitored simultaneously. The ion trace at m/z shows some intensity prior to taking coffee into the mouth, due to the volatile compounds in the breath-air. They display a rapid decrease of the volatile intensity with time, the swallow peak (particularly prominent at m/z 97) and the persistence of aroma once coffee was swallowing (afterodor).

4. Acknowledgments
We thank T. Märk, A. Jordan and D. Roberts for fruitful discussions.

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</tr>
<tr>
<td>ORAM David</td>
<td>University of East Anglia</td>
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</tr>
<tr>
<td>PEILOW Alan</td>
<td>Unilever R&amp;D Colworth</td>
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<td><a href="mailto:Alan.Peilow@unilever.com">Alan.Peilow@unilever.com</a></td>
</tr>
<tr>
<td>PETER Günter</td>
<td>Inficon AG</td>
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</tr>
<tr>
<td>POLLIEEN Philippe</td>
<td>Nestlé Research Center</td>
<td>Switzerland</td>
<td></td>
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<tr>
<td>PRAZELLER Peter</td>
<td>Pacific Northwest National Laboratory</td>
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<td>STEFELS Jacqueline</td>
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<td>VERUCCHI Roberto</td>
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<tr>
<td>YANAGIDA Hitoshi</td>
<td>Sanyu Plant Service Co, Ltd</td>
<td>Japan</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Affiliation</td>
<td>Country</td>
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<td>YERETZIAN Chahan</td>
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## Conference Program

### Saturday, Jan 18, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
</tr>
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<tbody>
<tr>
<td>15:00</td>
<td>REGISTRATION</td>
</tr>
<tr>
<td>15:00 - 16:30</td>
<td>snacks, coffee, drinks</td>
</tr>
<tr>
<td>18:30</td>
<td>Welcome Reception</td>
</tr>
<tr>
<td>19:00</td>
<td>Dinner</td>
</tr>
<tr>
<td>20:30</td>
<td>Inauguration A. Hansel &amp; T. Märk</td>
</tr>
</tbody>
</table>

Opening Lecture, J. Futrell, Presiding

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
</tr>
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<tbody>
<tr>
<td>20:45</td>
<td>A Historical Perspective: Flowing Afterglow to PTR-MS E. Ferguson</td>
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### Sunday, Jan 19, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>7:00 - 9:00</td>
<td>Breakfast</td>
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Sunday Morning: Environmental Science and Technology, A. Hansel, Presiding

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>9:00</td>
<td>Field Measurements with PTR-MS under different photochemical pollution situations J. Dommen</td>
</tr>
<tr>
<td>9:40</td>
<td>VOC Measurements of Urban Air in the Mexico City Metropolitan Area using the Proton Transfer Reaction Mass Spectrometer B. Knighton</td>
</tr>
<tr>
<td>10:20</td>
<td>Urban air measurement in Tokyo area using PTR-MS and comparison with GC-FID S. Kato</td>
</tr>
<tr>
<td>11:00 - 16:30</td>
<td>Discussion Forum</td>
</tr>
<tr>
<td>15:00 - 16:30</td>
<td>snacks, coffee, drinks</td>
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</tbody>
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Sunday Afternoon: Environmental Science and Technology, J. Dommen, Presiding

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:30</td>
<td>Applications of PTR-MS at JRC-Ispra in laboratory studies related to atmospheric chemistry N. Jensen</td>
</tr>
<tr>
<td>17:10</td>
<td>Deploying a PTR-MS onboard passenger aircraft (Project CARIBIC) for on-line monitoring of volatile organic compounds in the UTLS A. Zahn</td>
</tr>
<tr>
<td>17:50</td>
<td>PTR-MS measurements of acetonitrile, acetone and methanol: new implications and applications in the field of atmospheric chemistry R. Holzinger</td>
</tr>
<tr>
<td>19:00</td>
<td>Dinner</td>
</tr>
<tr>
<td>20:30 - 22:30</td>
<td>Presentation of Contributed Papers (Posters)</td>
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### Monday, Jan 20, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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</thead>
<tbody>
<tr>
<td>7:00 - 9:00</td>
<td>Breakfast</td>
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Monday Morning: Environmental Science and Technology, J. Williams, Presiding

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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</thead>
<tbody>
<tr>
<td>9:00</td>
<td>On-line analysis of VOC emissions from Sitka spruce (Picea sitchensis) S. Hayward</td>
</tr>
<tr>
<td>9:40</td>
<td>PTR-MS and GC-MS Analyses of Sesquiterpenes R. Rasmussen</td>
</tr>
<tr>
<td>11:00 - 16:00</td>
<td>Discussion Forum</td>
</tr>
<tr>
<td>15:00 - 16:00</td>
<td>snacks, coffee, drinks</td>
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</table>
## Monday Afternoon: Environmental Science and Technology, D. Oram, Presiding

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>16:00</td>
<td>Calibration and Application of PTR-MS for Biogenic VOC Measurements in a Deciduous Forest C. Ammann</td>
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<tr>
<td>16:40</td>
<td>Validation of Atmospheric VOC Measurements by PTR-MS J. de Gouw</td>
</tr>
<tr>
<td>17:20</td>
<td>coffee break</td>
</tr>
<tr>
<td>17:50</td>
<td>Proton Transfer Reaction Ion Trap Mass Spectrometry and other PTR-MS Research at PNNL M. Alexander</td>
</tr>
<tr>
<td>18:30</td>
<td>Development of an APCI-MS to investigate surface processes of atmospheric trace gases C. Guimbaud</td>
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<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
</tr>
</thead>
<tbody>
<tr>
<td>19:30</td>
<td>Dinner</td>
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<tr>
<td>21:30</td>
<td>Presentation of Contributed Papers (Posters)</td>
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## Tuesday, Jan 21, 2003

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>7:00</td>
<td>Breakfast</td>
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**Tuesday Morning: Environmental Science and Technology, C. Warneke, Presiding**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>9:00</td>
<td>Nitrous acid (HONO) measurements by PTR-MS A. Wisthaler</td>
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**Tuesday Morning: Food Technology, T. Märk, Presiding**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>9:40</td>
<td>Recent Research Using Proton Transfer Reaction Mass Spectrometry in Food Flavours, Plant Systems and Fragrances P. Dunphy</td>
</tr>
<tr>
<td>10:20</td>
<td>Model mouth analysis combined with Proton Transfer Reaction-Mass Spectrometry S. van Ruth</td>
</tr>
<tr>
<td>11:00</td>
<td>Discussion Forum</td>
</tr>
<tr>
<td>15:00</td>
<td>snacks, coffee, drinks</td>
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**Tuesday Afternoon: Food Technology, A. Boschetti, Presiding**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>16:00</td>
<td>PTR-MS studies to assess and monitor fruit quality during preservation S. Iannotta</td>
</tr>
<tr>
<td>16:40</td>
<td>Rapid determination of the microbial spoilage of meat D. Mayr</td>
</tr>
<tr>
<td>17:20</td>
<td>Discriminant analysis for PTR-MS Data in agroindustrial application F. Biasoli</td>
</tr>
<tr>
<td>20:00</td>
<td>Conference Dinner</td>
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<tr>
<td></td>
<td>A Homage to Werner Lindinger J. Futrell</td>
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## Wednesday, Jan 22, 2003

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>7:00</td>
<td>Breakfast</td>
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**Wednesday Morning: Food Technology, A. Peilow, Presiding**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>9:00</td>
<td>Progress and Prospects of PTR-MS in Food Science C. Yeretzian</td>
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<tr>
<td>9:40</td>
<td>Trace gas detection from fermentation processes I. Boamfa</td>
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<tr>
<td>10:20</td>
<td>A New Application of PTR-MS: Aroma Generation through the Maillard Reaction I. Blank</td>
</tr>
<tr>
<td>11:00</td>
<td>Discussion Forum</td>
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<tr>
<td>15:00</td>
<td>snacks, coffee, drinks</td>
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**Wednesday Afternoon: Medical Applications, A. Hansel, Presiding**

<table>
<thead>
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<th>Time</th>
<th>Session</th>
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<tbody>
<tr>
<td>16:00</td>
<td>Breath Monitoring of Propofol and its Volatile Metabolites in Real Time during Surgery using a Novel Mass Spectrometric Technique C. Mayhew</td>
</tr>
<tr>
<td>16:40</td>
<td>Breath Gas Analysis Using Proton-Transfer-Reaction Mass Spectrometry A. Amann</td>
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<tr>
<td>20:00</td>
<td>Dinner</td>
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<td></td>
<td>Concluding remarks A. Hansel &amp; T. Märk</td>
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## Thursday, Jan 23, 2003

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>7:00</td>
<td>Breakfast</td>
</tr>
<tr>
<td>9:00</td>
<td>Checkout and Departure</td>
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