Proton Transfer Mass Spectrometer

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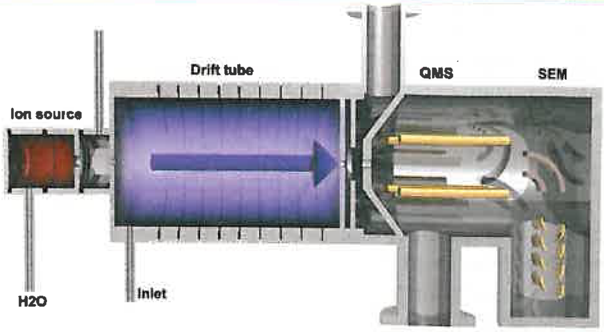
The first Proton Transfer Reaction Mass Spectrometer (PTR-MS) instrument was built ten years ago in our laboratories at the Institute of Ion Physics of the University of Innsbruck. In PTR-MS we use H_3O^+ ions to ionise volatile organic compounds (VOC) present in gaseous media, e.g. in air. This technique enables a variety of organic species in complex matrices to be monitored in real-time, with detection limits as low as a few parts per trillion, volume (pptv). In 1998 we founded the spin-off company Ionicon Analytik GmbH to provide this technique to a growing user community. Today we manufacture and sell PTR-MS instruments throughout the world. Our customers include noted multinational companies and renowned research institutions in the fields of environmental and food technology. This review covers the main principles of PTR-MS and shows key academic and commercial application areas in the market place.

Why PTR-MS?

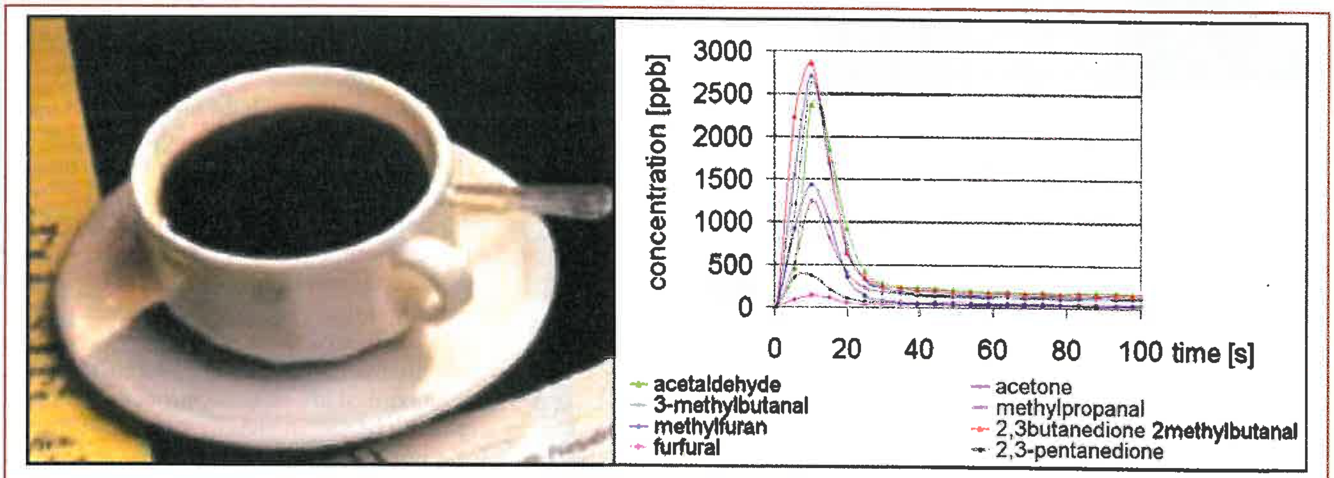
Conventional mass spectrometry (MS) is a well proven and highly sensitive technique for the identification and detection of organic pollutants. In simple terms, it works by separating organic molecules on the basis of their molecular masses. Molecules entering the mass spectrometer are ionised, usually by electron impact, and are then subjected to electromagnetic fields under whose influence ions with different mass/charge ratios will move in different trajectories. Thus the ionised molecules can be separated and individual molecules can be identified. That is the theory. Unfortunately, instead of forming a single ionised species, many molecules break down into smaller fragments, each of which is detected separately. This can result in one compound giving rise to a complex "mass spectrum". With a mixture of compounds entering the MS detector simultaneously, the final mass spectrum may be so complex that interpretation and quantification become difficult, if not impossible. The traditional solution to this problem has been to separate the compounds with a gas chromatograph (GC) before they are sent to a mass spectrometer. Unfortunately, GCs are inherently slow – a typical separation of just one sample could take 30 minutes – so while GC-MS is fine for analysing discrete samples or monitoring slowly changing situations, it cannot usually be regarded as a "real time" or on-line technique. PTR-MS can make the GC step unnecessary for many typical VOC analyses and achieve a response time measured in milliseconds. This opens a whole new range of possibilities in environmental monitoring, food science, odour analysis and medical applications.



▲ **Fig. 1:** Schematic representation of the PTR-MS instrument (QMS: quadrupole mass spectrometer; SEM: secondary electron multiplier)

How does it work?

The fundamental difference between a conventional MS and PTR-MS is the "soft ionisation" method used to ionise the organic molecules. PTR-MS uses chemical ionisation, in which the VOC molecules react with charged ions, in this case hydroxonium ions (H_3O^+) produced in an external ion source. The first PTR-MS instrument was developed at the University of Innsbruck [1-2] and is shown schematically in Figure 1. A glow discharge acts as an external ion source which produces H_3O^+ ions from pure water vapour. H_3O^+ primary ions enter the drift tube (DT), which is flushed continuously with ambient air, and undergo non-reactive



▲ **Fig. 2:** Release of flavour compounds in the head space air from freshly brewed coffee. With the PTR-MS technology you can see aroma as you taste it!

collisions with any of the common components in air (N_2, O_2, Ar, CO_2, ..). H_3O^+ ions transfer their proton exclusively to VOC molecules that have proton affinities higher than that of water, making reaction (1) exothermic, and forming VOCH+ ions with a collision efficiency of unity.

$$H_3O^+ + VOC \rightarrow VOCH^+ + H_2O \qquad (1)$$

The density of product ions [$VOCH^+$] in the DT follow pseudo first-order kinetics as expressed in equation (2), where t is the average reaction time the ions spend in the DT, and k is the reaction rate constant.

$$[VOCH^+] = [H_3O^+]_0(1 - e^{-k[VOC]t}) \approx [H_3O^+]_0\,[VOC]\,k\,t \qquad (2)$$

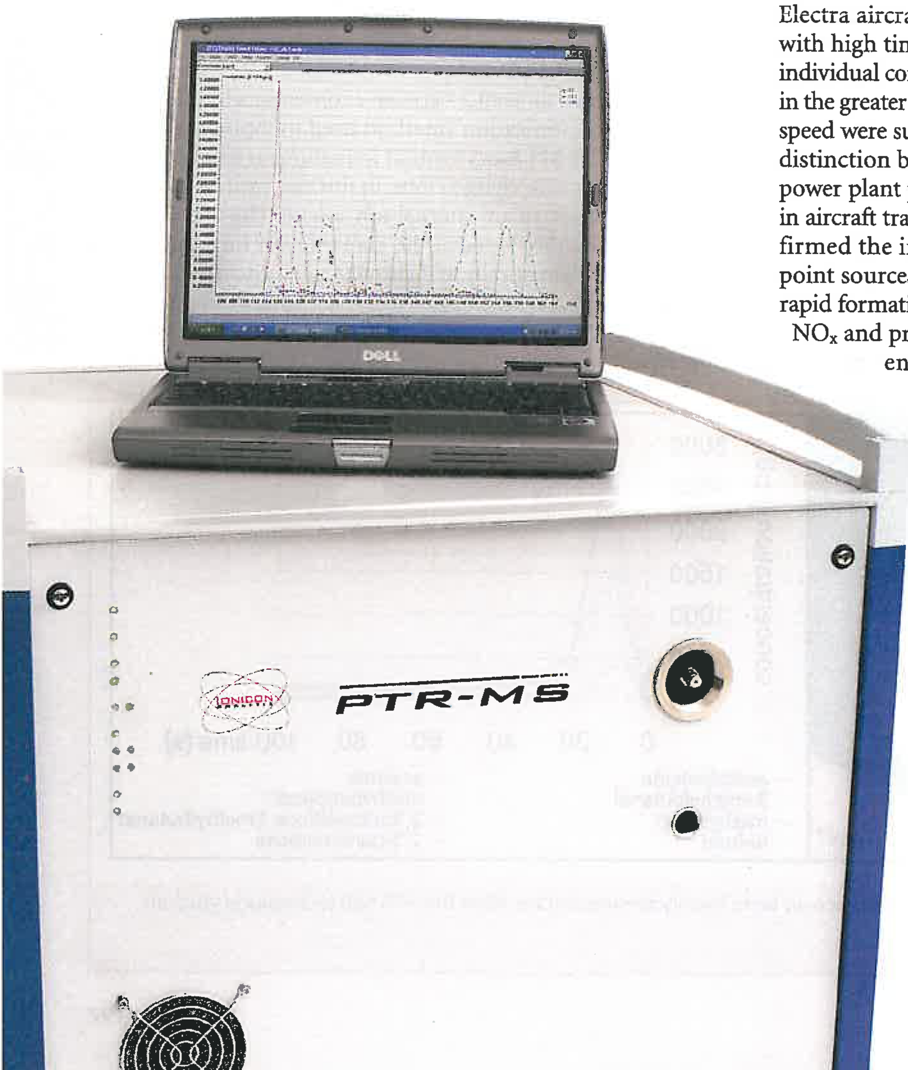
Primary and product ions are then detected by the MS in the usual way. The great advantage of this method, however, is that fragmentation of the product ions is very much reduced so the mass spectra produced are much easier to interpret and are more straightforward to quantify. This means that for many quantitative applications the preliminary GC separation becomes unnecessary.

Applications

The PTR-MS instrument has the key capability of being able to monitor and quantify complex mixtures of VOC in the gas phase such as alkenes, alcohols, aldehydes, aromatics, ketones, nitriles, sulphides and many others within seconds, with a detection limit of a few pptv. This means that one molecule out of 200 billion "air" molecules can be detected virtually in real time, without any time consuming work-up procedure. On the basis of these attributes it is possible to target a number of key academic and commercial application areas for exploitation of the technology. The most prominent amongst these are environmental, medical, and food/flavour applications. Fig. 2 shows an example from the food/flavour application; with PTR-MS you can visualise aroma in real time. In Fig. 2 you see the whole flavour release "film" and not just the fingerprint "snapshot" in the headspace air of freshly brewed coffee. With this technology a food flavourist can see the aroma as you taste it!

Over the last decade the PTR-MS technique has been used extensively in environmental sciences as a fast VOC sensor. Volatile organic compounds are emitted into the atmosphere from a wide variety of sources, both natural and anthropogenic. The photo-oxidation of VOC leads to ozone and aerosol formation, which are both major air pollutants, have adverse effects on health, and are significant factors for the Earth climate.

The Indian Ocean Experiment (INDOEX 1999) has offered the opportunity to study the influence of anthropogenic pollution in the tropical troposphere. In India and surrounding countries biofuel use and agricultural burning cause strong CO emissions. Ship and airborne PTR-MS measurements of organic trace gases in real time, over a broad spatial extent of the Indian Ocean, have turned out to be of great importance in detecting pollution outflow from India and in helping to quantify the relative amount of CO originating from biomass burning [3]. During the Texas Air Quality Study (TexAQS 2000) ambient air was analysed onboard the National Center for Atmospheric Research (NCAR) Electra aircraft. Molecular-level information of VOC obtained with high time resolution was essentially useful to characterise individual contributions of distinct sources for ozone production in the greater Houston area. On several flights, wind direction and speed were such that these airborne VOC measurements allowed distinction between anthropogenic petrochemical, urban, and power plant plumes. In-situ acetaldehyde measurements, taken in aircraft transects of the Houston metropolitan area, have confirmed the importance of propene emissions from localised point sources to the photochemical processing of NO_x and the rapid formation of ozone within short distances from co-located NO_x and propene emission sources. [4]. Supplementary references for further reading are available at www.uibk.ac.at/ionenphysik/umwelt.



◄ Fig. 3: Compact PTR-MS

History and development of IONICON ANALYTIK

Ten years ago we built the first Proton Transfer Reaction Mass Spectrometer instrument (PTR-MS) in Prof. Werner Lindinger's Laboratory at the Institute of Ion-Physics of the University of Innsbruck. In 1998 the key scientists involved in the development of the PTR-MS technology founded the company IONICON Analytik as a spin-off of the University of Innsbruck to provide this technique to a growing user community. Three years later in 2001, Prof. W. Lindinger died in a tragic accident. At the time of his death he was in Hawaii for the purpose of installing a PTR-MS instrument at the NOAA

Clean Air Baseline Station on the volcanic Mauna Loa mountain. Today the Ionicon Team (see www.ptrms.com) manufacture and sell PTR-MS instruments throughout the world. Now more than 70 instruments are used by many research groups and companies around the world, applying this technique in various fields. Our customers include noted multinational companies and renowned research institutions in the fields of environmental science and food technology.

Today, three different PTR-MS instruments are available. Besides the standard and high sensitive versions, the compact PTR-MS is the most recent development from Ionicon Analytik. The compact PTR-MS, the first commercially available configuration for more general applications, is pictured in Figure 3.

The future

In our business it is crucial to always be innovative. We therefore want to promote collaborative research between universities and industry. Ionicon Analytik is a partner in ISONET a Marie Curie Research and Training Network recently funded by the European Commission (http://imk-ifu.fzk.de/isonet). One objective of ISONET is to integrate an industrial partner to strengthen collaboration between industry and academia and to allow network trainees to use state-of-the-art and innovative facilities to carry out their research.

The goal of the 2nd International PTR-MS Conference next year (www.ptrms-conference.com) is to bring together active scientists and technologists involved in real-world mass spectrometric measurements of VOC from both academia and industry. The intent to found and organise such a biennial meeting was to promote discussion and stimulate the free exchange of ideas across disciplines, such as environmental sciences, food technology and medicine

About the author

Armin Hansel is Associate Professor in Physics at the University of Innsbruck. His research interests are ion-molecule-reactions and their application to trace gas analysis, which resulted in the development of the PTR-MS technique. In environmental physics he was involved in several international field programs. Armin is founding member of the academic spin-off company Ionicon Analytik GmbH.

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