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Foreword

In the past decades the need for quantitative and fast determinations of a variety of organic species in complex matrices (volatile organic compounds, VOCs) at ultralow concentrations continuously has pushed the limits of analytical chemistry. For a wide variety of real-world problems mass spectrometry has provided unique and competitive solutions. In general, 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. Unfortunately, instead of forming a single ionised species, many molecules break down into smaller fragment ions; this can result in one compound giving rise to a complex "mass spectral pattern". 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 enter a mass spectrometer (GC–MS). Unfortunately, GCs are inherently slow – a typical separation of just one sample can easily take 30 min – so while GC–MS is fine for analysing a single sample or monitoring slowly changing situations, it cannot usually be regarded as a "real-time" or on-line technique.

In order to overcome these problems a new technique called proton transfer reaction mass spectrometry (PTR-MS) has been developed about 10 years ago in our laboratories at the Institut für Ionenphysik of the Leopold Franzens Universität Innsbruck (LFUI) allowing quantitative on-line monitoring of volatile organic compounds. 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 (analyte) are reacted with charged ions, in most cases hydroxonium ions (H_3O^+) produced in an external glow discharge ion source operating in pure water vapour. H_3O^+ primary ions produced enter a drift tube, which is flushed continuously with ambient air, and undergo non-reactive collisions with any of the common components in air (N_2, O_2, Ar, CO_2, etc.). In contrast, H_3O^+ ions transfer their proton exclusively to VOC molecules that have proton affinities higher than that of water, making reaction (1) exothermic, and thus, yielding protonated analyte VOCs with unity collision efficiency.

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

The density of product ions $[\mathrm{VOCH}^+]$ at the end of the drift tube follows pseudo first order kinetics as expressed in Eq. (2), where t is the average reaction time the ions spend in the drift tube and k is the reaction rate constant.

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

Primary and product ions are then detected by a MS (e.g., quadrupole) in a conventional manner. The great advantage of this method, besides giving immediately absolute concentrations, is that fragmentation of the analyte molecule 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.

This novel technique enables a variety of organic species (such as alkenes, alcohols, aldehydes, aromatics, ketones, nitriles, sulphides and many others) in complex matrices to be monitored in real-time (within seconds), with detection limits as low as a few parts per trillion, volume (pptv). This means that one molecule out of 200 billion "air" molecules can be detected virtually in real-time, without any work up procedure. Thus, with PTR-MS it is possible to visualise the change of complex matrices in real-time, yielding a fingerprint "film" and not just a fingerprint "snapshot".

In 1998 a spin-off company called Ionicon Analytik GmbH (www.ptrms.com) was founded to provide this technique to a growing user community. Today more than 80 instruments are used throughout the world including noted multinational companies and renowned research institutions in the fields of environmental sciences, food technology and

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medicine. In particular, over the last five years 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. Ship and airborne PTR-MS measurements of organic trace gases in real-time turned out to be of great importance to detect pollution outflow and help quantify organic compounds originating from biomass burning or to characterise individual contributions of distinct sources for ozone production over urbane areas (also allowing to distinguish between anthropogenic petrochemical, urban, and power plant plumes).

The concept of a special issue to summarize the present status of this field arose spontaneously after a very successful first International Conference on Proton Transfer Mass Spectrometry in January 2003 in Igls, Austria, which was organized to honour the late Professor Werner Lindinger, the pioneer of PTR-MS who died in 2001 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. The undersigned were invited to serve as guest editors of this special edition. The number, variety and quality of the papers are themselves a testimony to the rapidly evolving field, the papers ranging from fundamentals and instrumentation of PTR-MS to a number of applications across disciplines such as environmental, food, flavour and life sciences. We are honoured by the part we could play in collecting, editing and publishing this special issue. We would like to thank Professor Helmut Schwarz for his support for this special issue from the beginning and we would like to acknowledge the authors for their cooperation throughout the process. A special thank goes to Dr. Wolfgang Sailer who supported us in the final round of the editing process.

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