

TECHNOLOGY OVERVIEW



PROTON TRANSFER REACTION - MASS SPECTROMETRY

THE SOLUTION FOR REAL-TIME TRACE GAS ANALYSIS



THE WORLD'S
LEADING
PTR-MS
COMPANY

WHAT IS PTR-MS?



PTR-MS

PTR-MS (Proton Transfer Reaction – Mass Spectrometry) technology enables real-time measurement of volatile organic compounds. Originally developed by scientists at the Institut für Ionenphysik at the University of Innsbruck, Austria this technology has been commercialized by IONICON Analytik.

PTR-MS allows the simultaneous real-time monitoring of volatile (organic) compounds (VOCs) like acetone, acetaldehyde, methanol, ethanol, benzene, toluene, xylene and many others present in ambient air. The IONICON PTR-MS instruments are known for their market-leading detection limits in the single-digit pptv-range and their real-time monitoring capabilities.

The first IONICON PTR-MS was sold in 1998 and in the following decade we have sold more than 150 PTR-MS units to the world's best scientists. PTR-MS has become the standard for ultimate real-time sensitivity in VOC monitoring and true to our mission we constantly strive to improve this leading technology and develop novel solutions for online trace gas analysis setting the benchmark in online mass spectrometry.

IONICON PTR-MS AT A GLANCE

- Market-leading real-time detection limit (ppqv-/pptv-range)
- No sample preparation (direct air sampling)
- Absolute VOC quantification without calibration
- Soft and efficient chemical ionization
- SRI: Switchable Reagent Ions (H_3O^+ , NO^+ , O_2^+)
- Discrimination of isobaric and isomeric compounds
- Quadrupole or time of flight mass spectrometry
- No gas supply or carrier gas necessary
- Robust, lightweight, easy to use

WHAT ARE THE ADVANTAGES OF PTR-MS?

ONLINE QUANTIFICATION WITHOUT CALIBRATION

PTR-MS provides absolute quantitative analysis in real-time (response time < 100 ms). The generation of the precursor reagent ions and the chemical ionization of the VOCs are individually controlled and spatially separated processes. This leads to constant and well defined conditions in the drift tube (unlike IMS, APCI-MS and similar technologies) making the determination of absolute concentrations possible without the use of gas standards.

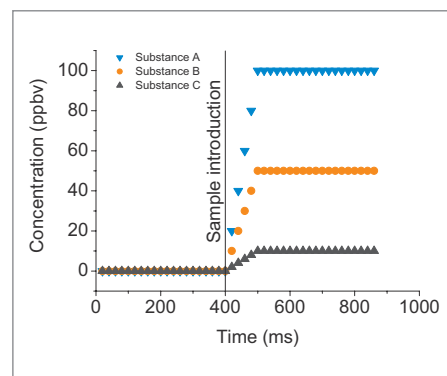


Figure 1: Real-time quantification of direct air samples

MARKET-LEADING LOW ONLINE DETECTION LIMIT

H_3O^+ ions do not react with any of the major components present in clean air due to their low proton affinity. Unlike other technologies (e.g. SIFT-MS) PTR-MS does not dilute low concentrated samples by a carrier gas and does not lose precursor ions on their way through a mass filter between the ion source and the drift tube. This makes PTR-MS very sensitive to trace gases in the sample air. Very high intensities of precursor ions and thus real single-digit pptv-range detection limits are the resulting benefits of our PTR-MS technology.

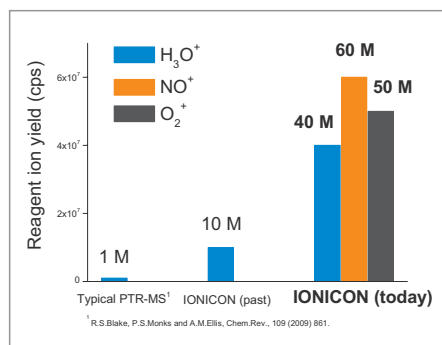


Figure 2: Very high precursor ion yield

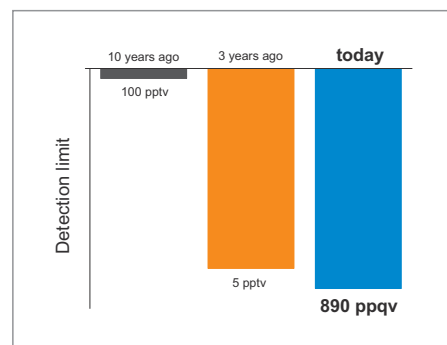


Figure 3: IONICON PTR-MS achieving detection limits in the ppqv-range

SOFT AND EFFICIENT CHEMICAL IONIZATION

Proton transfer from H_3O^+ is a soft ionization method, keeping fragmentation rates rather low as compared to e.g. electron impact ionization often used in GC-MS instruments, thus minimizing coincidences in the mass spectra and improving the identification capability.

SWITCHABLE REAGENT IONS (SRI)

By using not only H_3O^+ but also NO^+ and O_2^+ as reagent ions in an optional configuration of IONICON PTR-MS instruments, separation of isomeric compounds in real-time is now possible. Additionally, also substances that could not be ionized with H_3O^+ due to their low proton affinity are now detectable.

Note: Because of a highly sophisticated ion source design (hollow cathode discharge) we do not need a signal-diminishing mass filter to select these precursor ions, thus we can achieve outstanding sensitivity also for NO^+ and O_2^+ ionization.

NO SAMPLE PREPARATION

A major advantage of PTR-MS is that the samples do not need to be prepared before the measurement (e.g. pre-concentration or chemical separation procedures), thus whole-air samples can be introduced directly into the drift tube allowing for dynamic headspace sampling or VOC flux measurements.

THE LIBERTY TO CHOOSE BETWEEN QUADRUPOLE AND TIME OF FLIGHT MS

IONICON offers a broad range of different PTR-MS products and gives you the choice between different quadrupole mass filters or time of flight analyzers (allowing to distinguish isobaric product ions) for maximum flexibility and adaptation to your needs.

ROBUST AND EASY TO USE

No gas supply is necessary to operate an IONICON PTR-MS (i.e. for H_3O^+ and NO^+ reagent ions). Our instruments are light-weight (e.g. the portable Compact PTR-MS weighs only 55 kg) and space-saving which clearly puts us ahead of competing technologies. IONICON PTR-MS systems are often used for field campaigns or variable location measurements and can be operated in nearly every environment. Only 15 minutes after pressing the power-button, the Compact PTR-MS is ready to measure. Little maintenance and small operating costs complete the whole package.

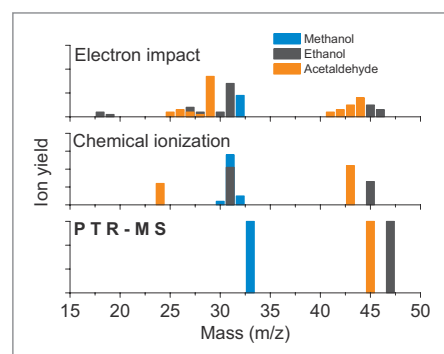


Figure 4: Soft and efficient Proton Transfer Reaction (PTR) ionization

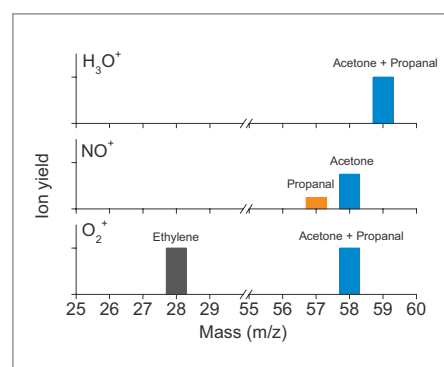


Figure 5: SRI allows for isomer separation and more compounds to be detected

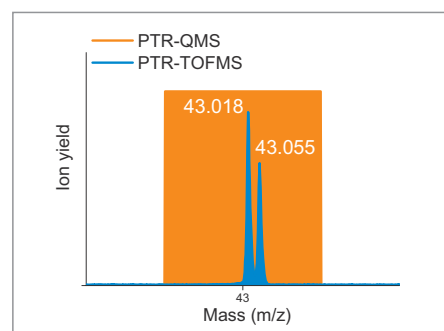
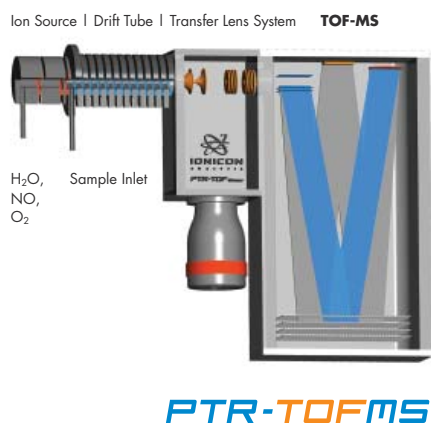
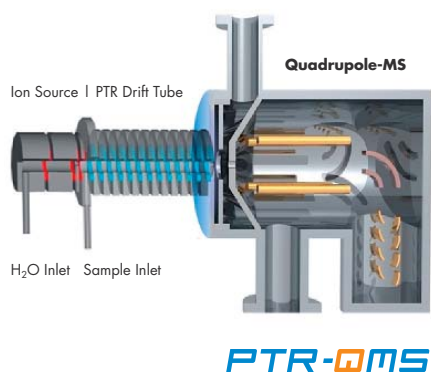


Figure 6: High-Resolution PTR-TOFMS Series

THE PTR-MS TECHNOLOGY

A IONICON PTR-MS SYSTEM CONSISTS OF
THREE MAIN PARTS:



- **Ion source:** Production of H₃O⁺ (optionally also NO⁺ and O₂⁺) ions at high purity levels (> 99%) from water vapor in a hollow cathode discharge.
- **PTR drift tube:** The VOC trace gases in the sampled air undergo (mostly) non-dissociative proton transfer from H₃O⁺ ions, which are injected into the drift tube via a specially designed inlet (pressure in the drift tube ~2.2mbar); alternatively charge and hydride ion transfer or association reactions of NO⁺ and O₂⁺ can be utilized.
- **Analyzing system:**

Quadrupole based systems: A quadrupole mass filter in conjunction with a secondary electron multiplier allows mass separation and detection of the ions.

Time of flight based systems: A high resolution time of flight (TOF) mass spectrometer separates the ions according to their mass to charge (m/z) ratio. The resolution is sufficient to distinguish between isobaric molecules and makes an unambiguous identification possible.

HOW DOES AN IONICON PTR-MS WORK?

The fundamental process in a PTR-MS instrument can be written as



This means that protonated water (H_3O^+) interacts with the trace gas (R). During this interaction a proton transfers from the hydronium to the trace gas molecule, which leads to a protonated and therefore ionized molecule (RH^+) and a neutral water molecule (H_2O). The proton transfer reaction (1) is energetically possible for all VOCs with a proton affinity higher than that of water (166.5 kcal/mol). Some other compounds with proton affinities below that of H_2O can be detected using our new switchable reagent ion (SRI) option.

ION SOURCE

For an efficient ionization via reaction (1) an abundant supply of H_3O^+ ions is necessary. In the IONICON PTR-MS instruments these primary ions are generated in a dedicated ion source that has been developed and was continuously improved to perfection over many years by our renowned experts.

In the ion source H_2O is broken down in a hollow cathode discharge. In a second step the fragments recombine to protonated water ions (H_3O^+) with very high purity (up to 99.5%) and can therefore be injected directly into the PTR drift tube without the need of an interconnected mass filter, which would lead to an inevitable loss of primary ions and eventually result in a worse detection limit.

PTR DRIFT TUBE

In the PTR drift tube the actual ionization process (1) of the trace gas molecules takes place. It can be easily derived that the PTR process (1) follows the equation

$$[\text{RH}^+] = [\text{H}_3\text{O}^+]_0 (1 - e^{-k[\text{R}]t}) \quad (2)$$

which can be simplified in good approximation to

$$[\text{RH}^+] \approx [\text{H}_3\text{O}^+]_0 [\text{R}]kt$$

$$\text{If } [\text{RH}^+] \ll [\text{H}_3\text{O}^+] \approx [\text{H}_3\text{O}^+]_0 = \text{const.} \quad (3)$$

In (2) and (3) $[\text{RH}^+]$ is the density of protonated trace constituents, $[\text{H}_3\text{O}^+]_0$ is the density of primary ions (in absence of the neutral reactants $[\text{R}]$), k is the reaction rate coefficient and t the average time the ions spend in the reaction region. The assumption (3) is justified, because only molecules with a proton affinity (PA) higher than the PA of water (166.5 kcal/mol) undergo a PTR reaction. As all common constituents of ambient air (N_2 , O_2 , Ar , CO_2 , etc.) have a lower PA than water, the air itself acts as a buffer gas and only volatile organic compounds (VOCs), which are usually present in very small densities, get ionized. Compared to electron impact ionization, the energy transfer in the PTR process is very low. This effectively suppresses fragmentation and leads to mass spectra that are easy to interpret.

DETERMINATION OF CONCENTRATIONS

The mass analyzing and detection system (Quadrupole mass filter or time of flight mass spectrometer) of the PTR-MS instrument delivers count rates (or currents) which are proportional to $[\text{RH}^+]$ and to $[\text{H}_3\text{O}^+]$. The average time t can be calculated from system parameters (drift voltage, pressure, temperature, etc.) and the reaction rate coefficient k can be found in literature for many substances (alternatively it can be calculated or experimentally determined). Knowing all necessary variables in (3) makes it possible to calculate the concentrations of VOCs in the measured volume of air without the need of gas standards via equation:

$$[\text{Concentration}]_{\text{ppbv}} = C * \frac{[\text{RH}^+]}{[\text{H}_3\text{O}^+]} \quad (4)$$

The highly sophisticated PTR-MS software automatically acquires and calculates all necessary data for equation (4) (constant C which includes k, t and a conversion factor as well as the ratio of the signal intensities) so that the user can monitor the absolute concentrations in ppbv or pptv of all measurable VOCs in real-time.

SWITCHABLE REAGENT IONS

PTR+SRI-MS
SWITCHABLE REAGENT IONS

Ionization with O_2^+ :

With O_2^+ compounds are ionized via charge transfer according to equation (5). The recombination energy of O_2^+ is 12.07eV, thus the electron transfer reaction is exothermic for analytes having an ionization energy below that value.



This means that with O_2^+ it is possible to ionize molecules that cannot be ionized via proton transfer from H_3O^+ because of their low proton affinity.

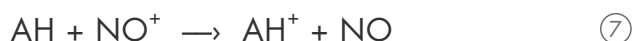


Ionization with NO^+ :

Ionization with NO^+ offers the great ability to identify and separate several isomeric molecules. When aldehydes react with NO^+ very likely hydride ion transfer takes place. Equation (6) describes this process and it can be easily seen that for this mechanism the product ions will appear on their molecular mass minus one amu (because of hydrogen loss).



For ketones (amongst other reactions) simple charge transfer occurs, which means that the product ions appear exactly on their molecular mass (7).



These facts lead to a situation that with NO^+ ionization, isomeric compounds appear on different nominal masses and are therefore distinguishable.

Note: NO^+ ionization is nearly as soft as proton transfer from H_3O^+ , which means that fragmentation is considerably suppressed. In addition to charge transfer and hydride ion transfer sometimes termolecular association reactions take place and can be used for unambiguous detection.

CONCLUSION

The combination of a highly sophisticated ion source, the efficient PTR ionization process and a state-of-the-art mass analyzing system in an IONICON PTR-MS instrument offer the possibility to monitor and quantify VOCs with IONICON PTR-MS instruments down to the single-digit pptv range while being compact, low cost in maintenance and reliable for a wide field of customers.



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