ULTRA-SENSITIVE SOLUTIONS
FOR REAL-TIME TRACE GAS ANALYSIS

TECHNOLOGIES OVERVIEW

PROTON TRANSFER REACTION - MASS SPECTROMETRY

SELECTIVE REAGENT IONIZATION - MASS SPECTROMETRY

IngenieríaAnalítica
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IONICON

PTR-MS

WHAT IS PTR-MS?

PTR-MS (Proton Transfer Reaction – Mass Spectrometry) enables simultaneous real-time detection, monitoring and quantification of volatile organic compounds (VOCs) such as acetone, acetaldehyde, methanol, ethanol, benzene, toluene, xylene and many others present in ambient air. Originally developed by scientists at the Institut für Ionenphysik at the University of Innsbruck, this technology has been commercialized by IONICON Analytik in 1998. Since then the IONICON PTR-MS instruments have been known for their outstanding sensitivities and market-leading detection limits in the single-digit pptv-levels and below.

SRI-MS

WHAT IS SRI-MS?

SRI-MS (Selective Reagent Ionization - Mass Spectrometry) represents IONICON's latest direct injection mass spectrometry technology: chemical ionization via different selectable reagent ions coupled to quadrupole or time-of-flight mass spectrometers. This feature is also optionally available as SRI or SRI+ add-on for all IONICON PTR-MS instruments. With SRI-MS all advantages of „classical PTR-MS" are preserved, while the number of analyzable substance classes is seriously enhanced, making SRI-MS instruments unique universal trace gas analyzers.

A SUCCESS STORY

The first IONICON trace gas analyzer was sold in 1998 and in the following 15 years we have marketed more than 250 PTR-MS units to the world's leading scientists. In the meantime PTR-MS has become the standard for ultimate real-time sensitivity in VOC monitoring. True to our mission we constantly strive to improve our technologies and develop novel solutions for real-time trace gas analysis setting the benchmark in real-time 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 highly efficient chemical ionization
- High reagent ion purity without the need for a signal-diminishing mass filter
- Quadrupole or time-of-flight mass spectrometry
- Discrimination of isobaric compounds
- No gas supply or carrier gas necessary, low running costs
- Robust, lightweight, easy to use

IONICON SRI-MS ADDITIONALLY OFFERS

- Selective Reagent Ionization (H_3O^+, NO^+, O_2^+, Xe^+ and Kr^+)
- Separation of several isomeric molecules
- Virtually no limitation of analyzable substance classes
- Very high reagent ion yields that result in ultra-high sensitivity

IONICON TRACE GAS ANALYSIS TECHNOLOGIES - SOLUTIONS FOR ALL YOUR MONITORING NEEDS!

FROM THE **WORLD'S LEADING** PTR-MS COMPANY.

MARKET-LEADING LOW REAL-TIME 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 or IMR-MS) PTR-MS does not dilute samples containing low analyte concentrations with a carrier gas and does not lose reagent ions on their way through a mass filter between ion source and drift tube. This makes PTR-MS very sensitive to trace gases in the sample air. Very high intensities of reagent ions and thus real single-digit pptv-range detection limits are the resulting benefits of the IONICON PTR-MS technology achieved through continuous improvements by IONICON engineers.

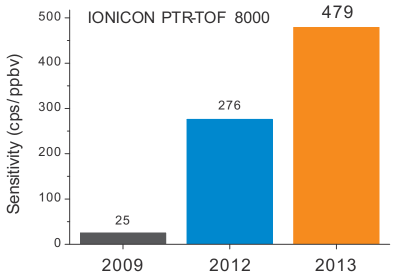


Figure **1**: Sensitivity evolution of the high mass resolution IONICON PTR-TOF 8000 (determined with certified gas standards)

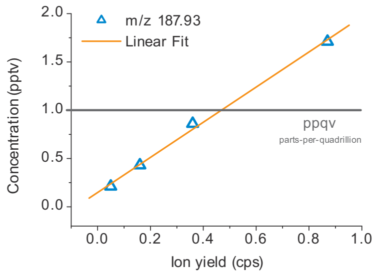


Figure **2**: Detection limits of a high mass resolution IONICON PTR-TOF 8000 in the ppqv-range (actual measurement results)

NO SAMPLE PREPARATION (DIRECT AIR SAMPLING)

A major advantage of PTR-MS and SRI-MS is that samples do not need to be prepared prior to the measurement (e.g. pre-concentration or chromatographic separation procedures), thus whole-air samples can be introduced directly which avoids any sampling and storage induced artifacts and is the key to real-time analysis (e.g. dynamic headspace sampling or VOC flux measurements).

REAL-TIME QUANTIFICATION WITHOUT CALIBRATION

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

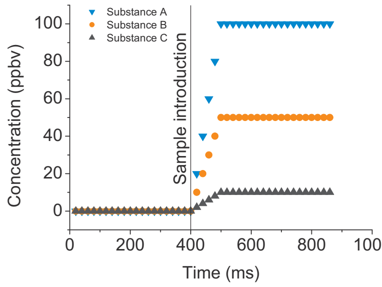


Figure **3** : Real-time quantification of direct air samples (schematic illustration)

CHEMICAL IONIZATION

Proton transfer from H_3O^+ is a soft ionization method, keeping fragmentation rates low (compared to e.g. electron impact ionization), thus minimizing the complexity of mass spectra and improving quantification and identification. The outstanding efficiency of proton transfer is one of the reasons why detection limits even in the ppqv region are possible with IONICON PTR-MS instruments.

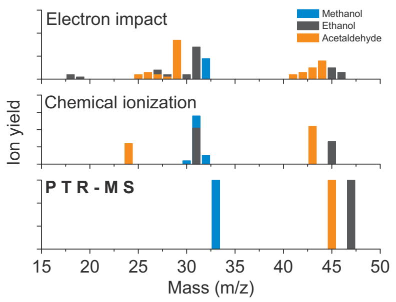


Figure **4**: Soft and efficient Proton Transfer Reaction (PTR) ionization (schematic illustration)

SELECTIVE REAGENT IONIZATION - MASS SPECTROMETRY (SRI-MS)

SRI-MS technology offers the freedom to choose the ideal reagent ion for virtually all fields of application. Where classic PTR-MS reaches its limitations, SRI-MS is the solution for your needs: choose among H_3O^+ (PTR), NO^+ and O_2^+ (SRI) or Kr^+ and Xe^+ (SRI^+) and enjoy utmost flexibility in one IONICON instrument. Separation of several isomeric compounds, detection of substances with low proton affinities and detailed investigations of the ion chemistry are just a few examples of the wide range of advantages of this new technology. Analyzing substances using different reagent ions adds a new dimension to the separation and identification capabilities of compounds. Note: Because of a highly sophisticated ion source design (hollow cathode discharge) there is no need for a signal-diminishing mass filter to select the reagent ions, which helps for achieving the outstanding sensitivity IONICON instruments are known for.

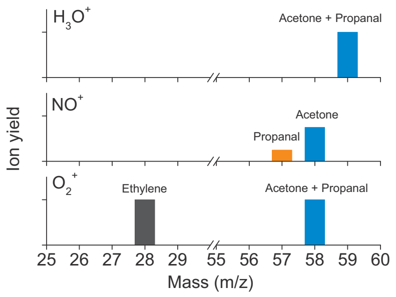


Figure **5**: SRI-MS allows for isomer separation and detection of more species: e.g. Ethylene (schematic illustration)

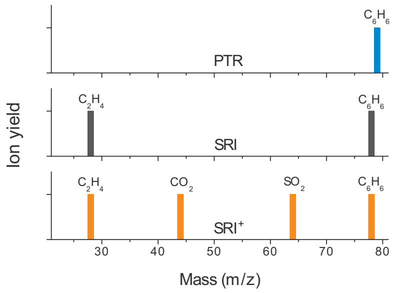


Figure **6**: SRI-MS analysis of a sample containing traces of C_2H_4, CO_2, SO_2 and C_6H_6 (schematic illustration)

THE LIBERTY TO CHOOSE BETWEEN QUADRUPOLE AND TIME-OF-FLIGHT (TOF) MASS ANALYZERS

IONICON offers a broad range of different PTR-MS and SRI-MS products and gives you the choice between quadrupole mass filters and time-of-flight analyzers for maximum flexibility and adaptation to your needs. Whereas quadrupoles are robust, cost-efficient and therefore ideal for selected compounds monitoring, TOF mass spectrometers acquire full mass spectra in a split-second and permit separation of isobars due to very high mass resolution, hence provide much more scientific insight.

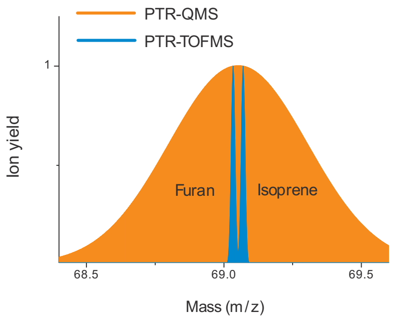


Figure **7**: Detection of two isobaric compounds with a PTR-QMS (unit mass resolution) and a PTR-TOF 8000 (schematic illustration)

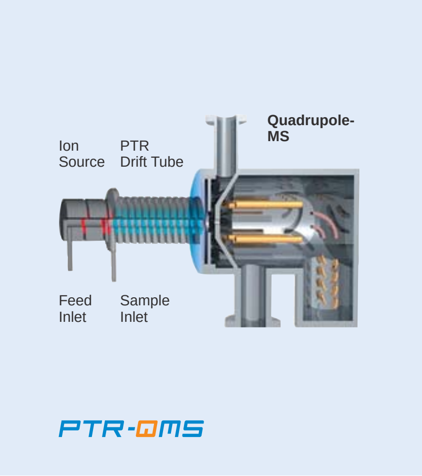
ROBUST, RELIABLE AND LOW IN RUNNING COSTS

Our instruments are light-weight, space-saving and low in energy consumption which clearly puts IONICON solutions ahead of competing technologies. Our trace gas analyzers are often used for field campaigns or variable location measurements and can be operated in nearly every environment: e.g. only 15 minutes after unpacking a PTR-QMS 300 is ready to measure. No gas supply is necessary to operate an IONICON PTR-MS instrument. For SRI-MS only minute amounts of gas (e.g. O_2 below 10 ml/min) are needed. Low maintenance and operating costs complete the whole package.

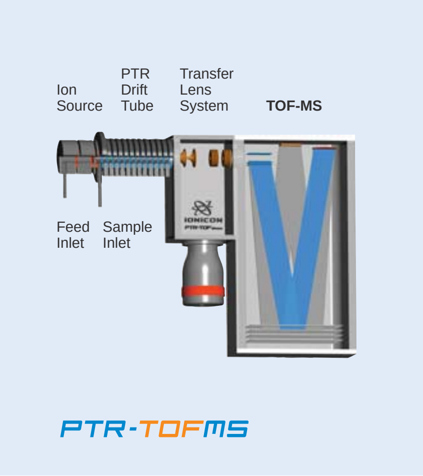
THE PTR-MS/SRI-MS TECHNOLOGIES

AN IONICON PTR-MS/SRI-MS SYSTEM CONSISTS OF **THREE** MAIN PARTS:

- **Ion source:** Production of the reagent ions at very high purity levels in a hollow cathode discharge.
- **Drift tube:** Trace gases in the sample air undergo either (mostly) non-dissociative proton transfer, charge and hydride ion transfer or association reactions, dependent on the selected reagent ions.
- **Analyzing system:**
  Quadrupole based systems: A quadrupole mass filter in conjunction with a secondary electron multiplier provides 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.



PTR-QMS



PTR-TOFMS

HOW DOES IONICON PTR-MS WORK?

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

$$H_3O^+ + R \rightarrow RH^+ + H_2O \qquad (1)$$

Protonated water (H_3O^+) interacts with the trace gas molecule (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). This proton transfer reaction (1) is energetically possible for all VOCs with a proton affinity higher than that of water (691 kJ/mol).

Ion source

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

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

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

which can be simplified in good approximation to

$$[RH^+] \approx [H_3O^+]_0 \, [R]kt \qquad \text{if}$$

$$[RH^+] \ll [H_3O^+] \approx [H_3O^+]_0 = \text{const.} \qquad (3)$$

In (2) and (3) $[RH^+]$ is the density of protonated trace constituents, $[H_3O^+]_0$ is the density of primary ions, k is the reaction rate coefficient and t the reaction time, i.e. the time the H_3O^+ ions spend in the reaction region. All common constituents of ambient air (N_2, O_2, Ar, CO_2 etc.) have a lower PA than water, and do not get ionized. The air itself acts as a buffer gas. Therefore assumption (3) is valid, since only volatile organic compounds (VOCs) with a proton affinity (PA) higher than the PA of water undergo a PTR reaction. This is the case for a large variety of VOCs, which are usually present in trace amounts. 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 $[RH^+]$ and to $[H_3O^+]$. 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:

$$[\text{Concentration}]_{\text{ppbv}} = C * \frac{[RH^+]}{[H_3O^+]} \qquad (4)$$

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 of all measured VOCs in real-time.

HOW DOES IONICON SRI-MS WORK?

The simplest form of ionization (charge transfer) with IONICON's novel SRI-MS technology is shown in equation (5): the trace compound B transfers an electron to the reagent ion A^+. This reaction is feasible when the ionization energy of A is close to or higher than the ionization energy of B.

$$A^+ + B \rightarrow A + B^+ \qquad (5)$$

However, as charge transfer ionization is a considerably „harder" ionization method compared to PTR ionization, fragmentation of the product ions is much more likely to occur. This is reflected in equation (6) where the reagent ion is again A^+, whereas the trace compound B consists of C + D. As a result of the reaction the charged fragment D^+ will be detected at the mass spectrometer.

$$A^+ + B \rightarrow A + C + D^+ \qquad (6)$$

One example, where both reaction pathways can be observed is the charge transfer ionization of benzene (C_6H_6) with Kr^+ as the reagent ion. The equations (7) and (8) show the two most abundant reactions, namely simple charge transfer (7) and charge transfer with hydrogen abstraction (8).

$$Kr^+ + C_6H_6 \rightarrow Kr + C_6H_6^+ \qquad (7)$$

$$Kr^+ + C_6H_6 \rightarrow Kr + H + C_6H_5^+ \qquad (8)$$

Special case: ionization with NO^+

Ionization with NO^+ even offers the great ability to identify and separate several isomeric molecules. When aldehydes react with NO^+ it is very likely that a hydride ion transfer reaction will take place. Equation (9) describes this process and it can be easily seen that for this mechanism the product ions will appear at their molecular mass minus one amu (because of hydrogen loss).

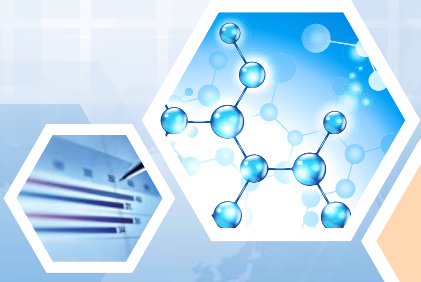
$$AH + NO^+ \rightarrow A^+ + HNO \qquad (9)$$

For ketones ionization mainly takes place via a simple charge transfer reaction, which means that the product ions appear exactly at their molecular mass (7).

$$AH + NO^+ \rightarrow AH^+ + NO \qquad (10)$$

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, offers the possibility to monitor and quantify VOCs down to and even below the single-digit pptv range while being compact, low cost in maintenance and reliable for a wide area of applications. The additional advantages of SRI-MS complement the unique PTR-MS technology and definitely make IONICON instruments the gold standard for universal real-time trace gas analysis.

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