What is Proton Transfer Reaction Mass Spectrometry (PTR-MS)?

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Proton Transfer Reaction Mass Spectrometry (PTR-MS) is the most widely used method for real-time monitoring of volatile organic compounds (VOCs) at low concentrations.

Advantages of PTR-MS

- Real-time and simultaneous detection of hundreds of VOCs
- Lowest available limits of detection (LODs) for real-time VOC analysis
- No sample preparation: The gaseous sample is directly analyzed
- Quantification of VOC concentrations, even without calibration with standards
- Soft chemical ionization reduces fragmentation and spectral complexity
- Detection of VOCs in liquid or solid samples via headspace analysis or other interfaces

The Principle of PTR-MS

The gaseous sample containing the VOCs to be analyzed (for example, ambient air) is sampled directly into the PTR mass spectrometer without any sample preparation.

The first stage of the PTR mass spectrometer is the PTR ionization source, where gas-phase VOC molecules are ionized by the transfer of a proton from H_3O^+ to the VOC molecules:

$$VOC + H_3O^+ \rightarrow VOC \cdot H^+ + H_2O$$

The VOC ions (VOC·H+) produced in this reaction are subsequently detected by a mass analyzer. The PTR-MS data can be used to identify and determine the concentrations of the VOCs in the sample.

Compounds That Can Be Detected and Monitored with PTR-MS

For the proton transfer reaction to occur, the VOC molecule must have a higher proton affinity than water. As shown in Figure 1, many VOCs satisfy this condition and are therefore detectable by PTR-MS. A great advantage of PTR-MS is that common air constituents (N_2, O_2) have lower proton affinity than water and do not react, thus no diluting buffer gas is required.

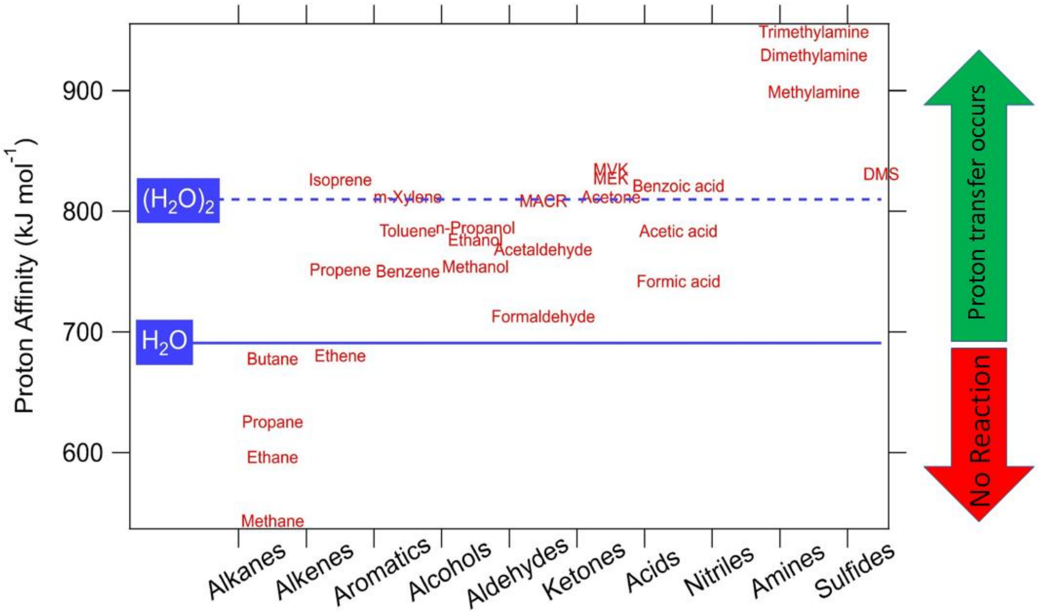

Figure 1. Proton affinities of some common VOCs. Compounds having higher proton affinity than water undergo proton transfer reactions with H_3O^+ and are detectable in real-time with PTR-MS.

It is also possible to use other reagent ions with the PTR-MS instrument, instead of H_3O^+. Common examples are O_2^+ and NO^+, but other ions are also possible. This capability extends the range of compounds that can be detected to include VOCs that have a proton affinity lower than water. Fast switching between reagent ions can also be used to separate isomeric compounds (molecules containing same atoms, but having different conformation), which have different reactivity with the various reagent ions.

The Main Components of a PTR Mass Spectrometer

Sampling Inlet. The sampling inlet draws the gas-phase analyte molecules directly into the proton transfer reaction cell. Inlet designs vary and must consider factors such as inertness of materials and flow rate. The inlet line may be heated to facilitate the detection of “sticky” VOCs. Unheated inlets are preferred for the analysis of VOCs that are easily degraded by temperature.

Ion Source. The H_3O^+ reagent ions are generated in the ion source. A common design uses a hollow cathode discharge to produce H_3O^+ ions from humidified air. Spurious ions generated in the discharge in addition to H_3O^+, e.g. H_2O^+, OH^+, and O^+, undergo efficient reactions with the water that also lead to H_3O^+, such that the equilibrium ion population is very pure hydronium ions (H_3O^+). Electric fields move the generated H_3O^+ ions from the ion source to the proton transfer reaction cell, where the ions interact with gaseous analyte molecules exiting the sampling inlet.

Proton Transfer Reaction Cell. The reactions between H_3O^+ ions and VOCs occur within a volume that has stable and controlled electric fields, temperature, and pressure.

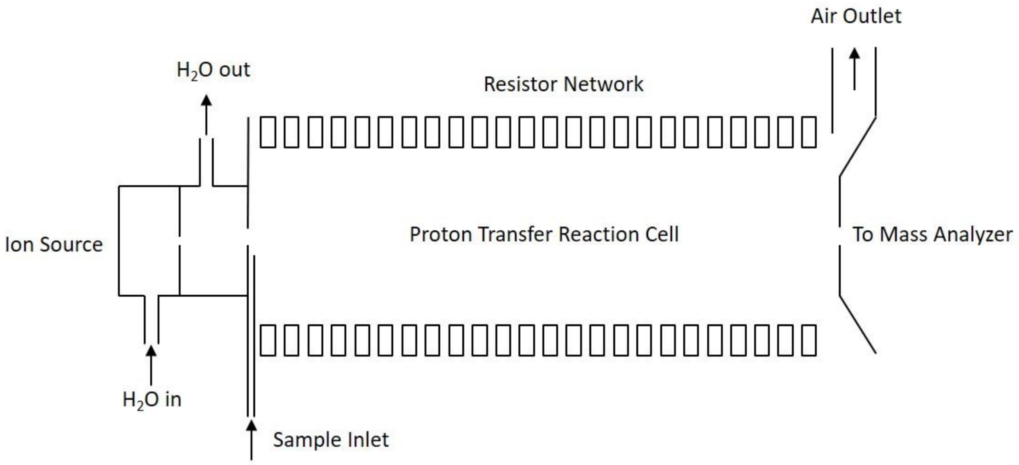

Figure 2 Schematics of a traditional PTR-MS instrument consisting of an ion source, an ion source gas port, and a drift reactor. A distinguishing feature of this PTR-MS design is that the drift tube is constructed by a series of ring electrodes. This axial field can be used to control the reactant ion population.

This tunability and stability are critical to provide absolute quantification of VOC concentrations in real-time. Pressure in the proton transfer reaction cell is typically on the order of 2 mbar. Electric fields inside the chamber move the reagent H_3O^+ ions and the product ions (i.e. the protonated VOCs) along the "drift axis" towards the detector region. The quantity E/N is conveniently employed to describe the conditions in the reaction chamber, where E is the electric field along the drift axis and N is the gas number density. Typical values of E/N are in the range 80-150 Td. Conventional designs include only a linear, DC field along the drift axis. The TOFWERK Vocus reaction cell uniquely superimposes oscillating RF fields on top of a DC field to increase net transmission of ions out of the reaction chamber and therefore improve sensitivity.

Ion Focusing Interface. The ion focusing interface must efficiently transmit ions from the proton transfer reaction cell to the mass analyzer, while reconciling the pressure difference between the reaction cell (e.g., 2 mbar) and the lower pressure mass analyzer (e.g., 1e-6 mbar). The pressure drop from the reaction cell to the mass analyzer occurs across a succession of differentially pumped vacuum stages, each having lower pressure. Ion optics are used to steer and focus the ions through these stages. Designs vary and may include both static steering and focusing elements and RF components, such as quadrupole ion guides.

Mass Analyzer. Analyte ions are detected by a mass analyzer that enables identification of VOCs based on their mass-to-charge ratio (m/Q) and determination of their concentrations based on recorded signal intensity. The first PTR-MS instruments used quadrupole mass analyzers, which are filtering devices that allow ions of a single m/Q to strike the detector at any moment. A user may monitor specific m/Q values of interest, or scan across an entire range of m/Q to produce a complete mass spectrum. Quadrupole mass analyzers typically have unit mass resolution, meaning they cannot resolve ions that have the same nominal mass-to-charge ratio. A few academic groups have explored the use of ion trap mass analyzers for PTR-MS, but this has not been offered commercially.

Use of time-of-flight (TOF) mass analyzers has become common in recent years. TOF mass analyzers separate ions based on differences in their velocities after acceleration by a fixed potential. TOF mass analyzers inherently measure all mass-to-charge ratios simultaneously, and therefore excel for any PTR-MS analyses that intend to measure many different VOC species. Further, TOF mass analyzers can have much higher mass resolving power than quadrupole mass analyzers. The TOFWERK Vocus PTR-TOF has the highest available mass resolving power of any commercial PTR-MS, thus providing the possibility to separate many isobaric VOCs and to derive the sum formula of recorded compounds. TOF-based PTR-MS systems also provide better time resolution and mass range (>1000 Th) than quadrupole-based systems.

A Historical Perspective of PTR-MS

PTR-MS has its origins in the so called “flowing afterglow” technique, which was pioneered by Ferguson and coworkers in the 1960s for use in studies of ion-molecule reactions. In this technique, ions are generated via a discharge in a gas. The bright glow of the discharge extends from the ion source region into an adjacent region containing a flow of inert buffer gas mixed with trace amounts of neutral molecules. Ions in this afterglow react with the neutral molecules, thus allowing studies of ion-molecule reactions.

The first evolution of the afterglow techniques was the development of the selective ion flow tube (SIFT) technique[2] in the 1970s. SIFT overcomes a weakness of the original afterglow method which has no ion selection prior to reaction with the neutral molecules. In SIFT, a quadrupole filter transmits only ions of a specific mass-to-charge ratio into the flow tube for reaction with the neutral molecules. Nowadays, SIFT is used both for investigations of ion-molecule reactions and for analyzing trace gases in air. In the latter employment, known as SIFT-MS, the neutral molecules are the analytes of interest, and a mass analyzer is used for detection after the reaction flow tube reactor.

PTR-MS is a further evolution, introduced by Lindinger and coworkers[3] in the 1990s. PTR-MS adds two innovations. Rather than select reagent ions with a quadrupole, the reagent ions are produced with very high purity by a hollow-cathode discharge. Secondly, the flow tube is replaced by a relatively short drift tube, using an electric field instead of a carrier gas to transport ions. The net result is a gain of several orders of magnitude in the detection sensitivity for VOCs compared to SIFT-MS[4].

References

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