



A Review On Proton Transfer Reaction Mass Spectroscopy

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ABSTRACT

Proton transfer reaction mass spectrometry (PTR-MS) allows for real time, online determination of absolute concentrations of volatile organic compounds (VOCs) with a high sensitivity and low detection limits (in the parts per trillion ranges). The technique utilizes H₃O⁺ ions for proton transfer reactions with many common VOCs while having little to no reaction with any constituents commonly present in it are detected by PTR- TOF .It combines the desirable attributes of high sensitivity and short integration times with good precision and accuracy . Medical applications by means of breath analysis allow the monitoring of metabolic processes in the human body, and examples of food research include investigations of volatile organic compound (VOC) emissions from fruit, coffee and meat. Investigations of VOC emissions from decaying bio-matter and on-line monitoring of the diurnal variations of VOCs in ambient air are typical examples of Environmental applications.

Keywords: PTR-MS, Volatile organic compounds, PTR -TOF.

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Received 12 March 2019, Accepted 15 June 2019

Please cite this article as: Bhavyasri K *et al.*, A Review On Proton Transfer Reaction Mass Spectroscopy . American Journal of Pharmacy & Health Research 2019.

INTRODUCTION

Proton transfer reaction mass spectrometry (PTR - MS) was first developed at the Institute of Ion Physics of Innsbruck University in the 1990s. Nowadays, PTR - MS is a well-developed and commercially available technique for the online monitoring of trace volatile organic compounds (VOCs) down to parts per trillion by volume (pptv) level. PTR - MS has some advantages such as rapid response, soft chemical ionization (CI), absolute quantification, and high sensitivity. In general, a standard PTR - MS instrument consists of external ion source, drift tube, and mass analysis detection system. Figure 1 illustrates the basic composition of the PTR - MS instrument constructed in our laboratory using a quadrupole mass spectrometer as the detection system¹. Volatile organic compounds (VOCs) are a large group of compounds with atmospheric lifetimes from seconds to months². Volatile organic compounds (VOCs) are emitted into the atmosphere from both natural and anthropogenic sources and have lifetimes ranging from minutes to months. This diverse group of compounds is of interest in the troposphere because of their role in ozone (O₃) production, aerosol formation and controls on regional air quality⁵. Commercially available PTR-MS instruments have response time of about 100 ms and reach a detection limit in the single digit pptv region. Established fields of application are environmental research, food and flavor science, biological research, medicine etc⁶.

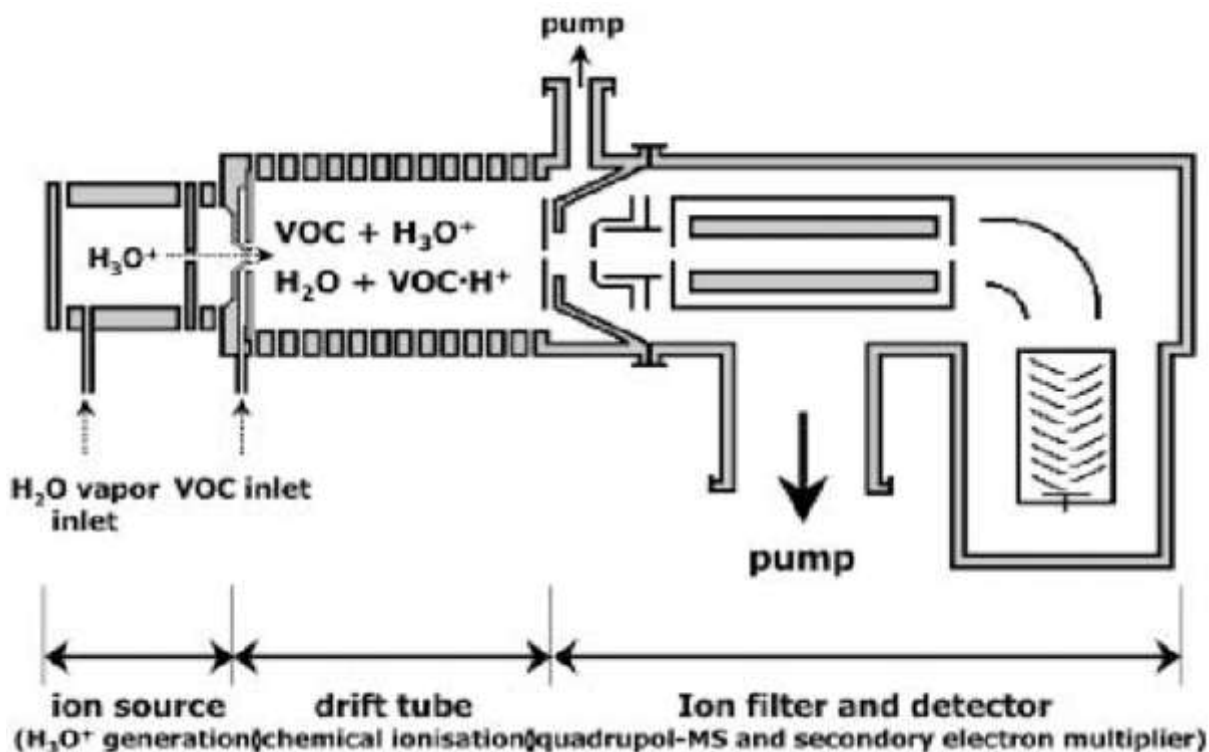
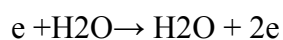
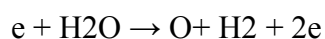
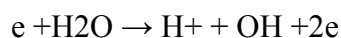


Figure: 1 PTR-MS Instrumentation

Ion Sources

PTR - MS is the special CI mode through well - controlled proton transfer reaction, in which the neutral molecule M may be converted to a nearly unique protonated molecular ion MH⁺. This ionization mode is completely different from traditional mass spectrometry (MS) where electron impact (EI) with energy of 70 eV is often used to ionize chemicals like VOCs. Although the EI source has been widely used with the commercial MS instruments most coupled with a variety of chromatography techniques, these MS platforms have a major deficiency: in the course of ionization, the molecule will be dissociated to many fragment ions. This extensive fragmentation may result in complex mass spectra especially when a mixture is measured. If a chromatographic separation method is not used prior to MS, then the resulting mass spectra from EI may be so complicated that identification and quantification of the compounds can be very difficult. PTR - MS instrument, the hollow cathode discharge is served as a typical ion source, although plane electrode direct current discharge and radioactive ionization sources¹. In commercial PTR-MS instruments water vapor is ionized in a hollow cathode discharge. Due to the high purity of the primary ions a mass filter between the ion source and the reaction drift tube is not necessary and the H₃O⁺ ions can be injected directly. The absence of this mass filter in turn greatly reduces losses of primary ions and leads eventually to an outstandingly low detection limit of the whole instrument. In the reaction drift tube a vacuum pump is continuously drawing through air containing the VOCs one wants to analyze. At the end of the drift tube the protonated molecules are mass analyzed (Quadrupole or Time-of-flight mass spectrometer) and detected⁶.



The above ions are injected into a short source drift region and further react with H₂O ultimately leading to the formation of H₃O⁺ via ion molecule reactions. Instead of H₃O⁺, other primary reagent ions, such as NH₄⁺, NO⁺, and O₂⁺. Because the ion chemistry for these ions is not only proton transfer reaction, the technique is sometimes called CI reaction¹.

Drift Tube

The drift tube consists of a number of metal rings that are equally separated from each other by insulated rings. Between the adjacent metal rings, a series of resistors is connected. A high voltage power supplier produces a voltage gradient and establishes a homogeneous electric field along the axis of the ion reaction drift tube. The primary H₃O⁺ ions are extracted into the ion

reaction region and can react with analyte M present in the sample air, which through the inlet is added to the upstream of the ion reaction drift tube. According to the values of proton affinity (PA) (see Table -1), the reagent ion H_3O^+ does not react with the main components in air like N_2 , O_2 and CO_2 . In contrast, the reagent ion can undergo proton transfer reaction with M as long as the proton affinity of M exceeds that of H_2O ¹⁶.



Thus, the ambient air can be directly introduced to achieve an online measurement in the PTR - MS operation. Due to the presence of electric field, in the reaction region, the ion energy is closely related to the reduced field E/N , where E is the electric field and N is the number density of gas in the drift tube. In a typical PTR - MS measurement, E/N is required to set to an appropriate value normally in the range of 120 ~ 160 Td (1 Td = 10 – 17 Vcm²/molecule), which may restrain the formation of the water cluster ions $H_3O^+ (H_2O)_n$ ($n = 1 - 3$) to avoid the ligands switch reaction with analyte⁶.



However, a higher reduced - field E/N can cause the collision - induced dissociation (CID) of the protonated products, thereby complicating the identification of detected analytes¹.

Table 1: Proton Affinities of Some Compounds⁵

| Compound | Molecular compounds | Proton affinities |
|--------------|---------------------|-------------------|
| Helium | He | 177.8 |
| Neon | Ne | 198.8 |
| Argon | Ar | 369.2 |
| Oxygen | O_2 | 421 |
| Water | H_2O | 691 |
| Acetonitrile | CH_3CN | 779.2 |
| Acetone | CH_3COCH_3 | 812 |
| Benzene | C_6H_6 | 750.4 |
| Ethanol | C_2H_5OH | 776.4 |

Mass Analyzer

A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output. The 2 types of mass analyzers used are Quadrupole mass analyzer and Time of flight mass analyzers⁷.

Quadrupole Mass Analyzer

The DC bias will cause all the charged molecules to accelerate and move away from the center line, the rate being proportional to their charge to mass ratio. If their course goes off too far they

will hit the metal rods or the sides of the container and be absorbed. So the DC bias acts like the magnetic field B of the mass spec and can be tuned to specific charge to mass ratios hitting the detector. The two sinusoidal electric fields at 90 orientations and 90 degrees phase shift will cause an electric field which oscillates as a circle over time¹⁷. So as the charged particles fly down toward the detector, they will be traveling in a spiral, the diameter of the spiral being determined by the charge to mass ratio of the molecule and the frequency and strength of the electric field. The combination of the DC bias and the circularly rotating electric field will be the charge particles will travel in a spiral which is curved. So by timing the peak of the curved spiral to coincide with the position of the detector at the end of the quadrupole, a great deal of selectivity to molecules charge to mass ratio can be obtained⁶.

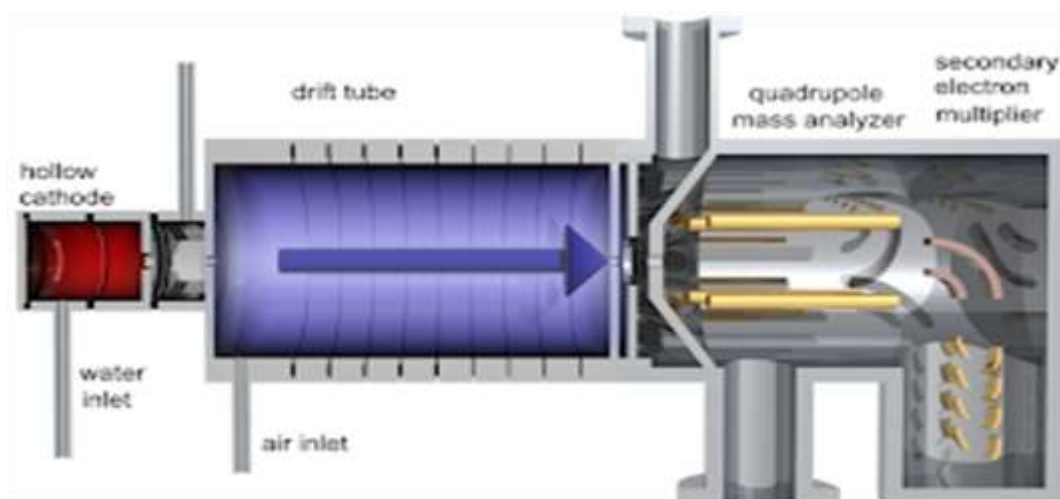


Figure: 2 PTR- Quadrupole Mass Analyzer

Time of Flight Mass Analyzer

TOF Analyzers separate ions by time without the use of an electric or magnetic field. TOF is similar to chromatography, except there is no stationary or mobile phase; instead the separation is based on the kinetic energy and velocity of the ions. It uses fixed voltages and does not require a magnetic field. Higher mass will reach the detector first. Ions produced acquire different velocities depending on the masses¹¹.

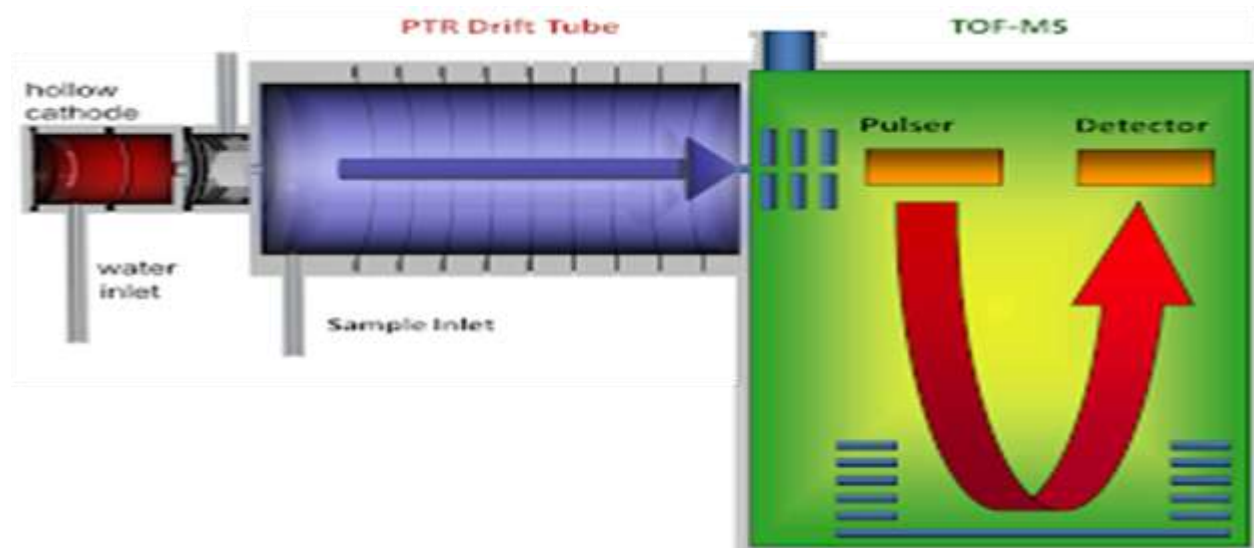


Figure: 3 PTR- TOF mass analyzer

APPLICATIONS

- Field of atmospheric monitoring.
- Some of the volatile compounds those are toxic to human.
- ROOT ANALYSIS: *Diuraphis noxia* with *Arabidopsis* roots resulted in the rapid release of 1, 8-cineole, a monoterpene.
- Local emissions from specific plants like methanol, acetaldehyde, ethanol, acetone, acetic acid, isoprene, toluene, jasmonic acid etc which are emitted from Mediterranean helm oak (*Quercus ilex*)¹⁵.
- Tropical forests – (reactive trace gases) isoprene and degradation products like methyl vinyl ketone, methacrolien and isoprene hydro peroxides.
- Breath gas analysis: a sweet, fruity breath aroma originates from high levels of acetone in patients with diabetes.
- Breathe markers that can be used to detect a specific histological type of lung cancer.
- Monitoring the gas of fermentations in the biopharmaceutical industry allows microbial activity.
- Breath marker for smoking is acetonitrile.
- Analysis of “sticky” volatile compounds.
- Detecting three VOCs that are common in human urine: methanol, acetaldehyde, and acetone¹⁰.

- To assess the freshness of meat in air packing conditions: (aerobic bacteria – Enterobacteria, Pseudomonas produce protonated diethyl sulphide, thioacetic acid methyl ester)¹.
- Quantitative long-term measurements of VOC concentrations of methanol and acetone annual cycle at a boreal forest site¹⁴.
- Analysis of volatile compounds in olive fruits⁴.
- The chemical compounds of interest released from *T. pseudomonana* were influenced by the growth phase of the diatoms can be analyzed⁷.
- Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences⁵.
- Rapid online tool for biogas VOCs monitoring in support of the development of Solid Oxide Fuel Cells⁹.

CONCLUSION

PTR-MS is a high sensitivity, rapid and non-invasive “sensor” which can be used for the monitoring of volatile compounds. It has been successfully applied to a variety of fields including environmental science, food science and technology, plant physiology and medical science. In some cases PTR-MS has been used for the identification and quantification of relevant compounds but it can also be used as rapid highly specific MS.

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