

Advantages of PTR-MS and PTR-TOF-MS techniques for measuring volatile organic compounds (VOCs)

Miguel Portillo-Estrada

Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, Tartu 51014, Estonia, e-mail: miguel.portillo@emu.ee

The Proton Transfer Reaction Mass Spectrometer (PTR-MS) was developed by the University of Innsbruck (Austria) in the mid 1990s (Hansel et al., 1995; Lindinger et al., 1998). The device uses the chemical ionization to protonize volatile compounds with a proton affinity higher than H₂O (691 kJ/mol) (Blake et al., 2009). The major components of ambient air have a lower proton affinity than H₂O (e.g. N₂, O₂, CO₂, etc), thus the primary ion H₃O⁺ only reacts with traces gases like volatile organic compounds. Therefore, PTR-MS technique can detect a large list of compounds such as aldehydes (e.g. acetaldehyde), ketones (e.g. acetone), aromatic compounds (e.g. benzene), alcohols (e.g. methanol and ethanol), sulphur compounds (e.g. dimethyl sulfide), unsaturated compounds (e.g. isoprene and α pinene), nitriles (e.g. acetonitrile), esters, acids and compounds with multiple functional groups (e.g. methyl salicylate). PTR-MS is a very reliable instrument for real-time trace gas monitoring. Since its release to the market, the instrument has improved its sensitivity and limit of detection achieving the pptv (parts per trillion by volume) level.

PTR-MS technique uses a method for soft ionization of molecules in the gas phase: pure water vapor enters in the ion source hollow cathode, where it is protonized to H₃O⁺. Then, the protons are transported to a drift tube where they meet and react with the air sample. The ionization of trace gases is very effective because of the high purity (~ 99 %) and much larger concentration of H₃O⁺ compared to trace gases. In addition, the molecule fragmentation is minor compared to other ionization methods like electron impact ionization. This creates mass spectra trustable and easily interpretable.

PTR-MS device performs the separation of protonized compounds by mass by a quadrupole mass filter. This technique is limited by its low mass resolving power and different compounds within one nominal mass could not be discriminated. For example, at nominal mass 69, protonated furan (m/z = 69.03349) and protonated isoprene (m/z = 69.06988) would appear as a single signal.

This problem was further solved after the development of time-of-flight (TOF) mass detection technique. The first PTR-TOF-MS prototype was presented in 2007, and commercially released in 2008. In contrast to quadrupole PTR-MS instruments, the time-of-flight version produces continuous mass spectra. This is because TOF detection is based on the time (a continuous variable) that molecules take in "flying" a known distance helped by repulsive voltages. Thanks to this advanced mass detection system; molecules of different molecular mass hit the detector at different times. Then, it is possible to discriminate different peaks within multiplets (isobaric compounds) and take in account the decimals of the molecular masses to identify the compounds.

Unfortunately, isomeric compounds (molecules with the same molecular formula but different chemical structures) cannot be distinguished. These compounds are of special interest to plant biology, perfume industry and air quality and other complementary techniques like VOC trapping and further gas chromatography analysis must be performed to detect the range of isomeric compounds. The same problem occurs with geometric isomerism.

In PTR-MS technology, the primary ion can also be switched to NO^+ or O_2^+ to investigate the range of mass spectrum near to the H_3O^+ signal, because when H_3O^+ is the primary ion, the signal is saturated at the neighboring masses to $m/z = 19$ (H_3O^+) and $m/z = 37$ (water cluster H_5O_2^+).

In conclusion, the quadrupole and TOF technologies developed in these last years have widened the possibilities of gas trace analysis; in particular for animal and plant biology, medicine, food chemistry, atmospheric chemistry, etc. For example, the on-line data acquisition permits to monitor animal and plant responses through volatile compound emissions (e.g. herbivory, light, exposition to compounds, stresses or metabolic reactions). Also, the high time resolution (smaller to 100 ms in PTR-TOF-MS) of analysis allows using these instruments for eddy-covariance emission and deposition flux measurements setups (where 10 Hz data is needed).

References

- Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., Lindinger, W., 1995. Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level. *International Journal of Mass Spectrometry and Ion Processes* 149, 609-619.
- Lindinger, W., Hansel, A., Jordan, A., 1998. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research. *International Journal of Mass*

Spectrometry and Ion Processes 173(3), 191-241.

Blake, R. S., Monks, P. S., Ellis, A. M., 2009. Proton-transfer reaction mass spectrometry. Chemical Reviews 109(3), 861-896.