Advantages of Proton Transfer Reaction – Mass Spectrometry (PTR-MS) in the Analysis of Potentially Dangerous Substances

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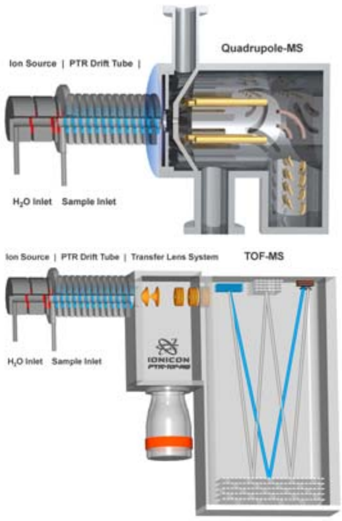
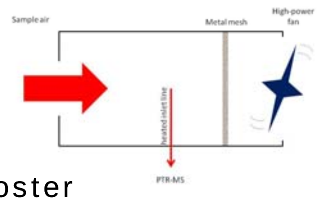


Abstract

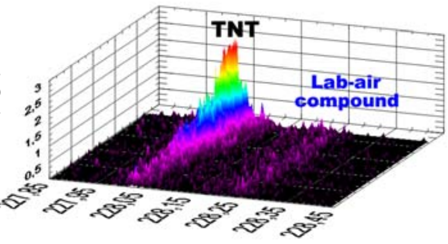
Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is an innovative technology invented and developed by scientists of the "Institut für Ionenphysik" at the Leopold-Franzens University in Innsbruck and made commercially available by the spin-off company IONICON Analytik GmbH. Details about the technique have been described elsewhere (e.g. [1], [2] and very recently [3]). In short, in a hollow cathode ion source hydronium ions (in the novel "SRI" mode also NO^+ or O_2^+) are produced at very high purity levels (up to 99.5%) and afterwards injected into a drift tube where the actual ionization process takes place via proton transfer from the hydronium (or charge transfer from NO^+ or O_2^+) to the trace constituents. Finally either a quadrupole or a time-of-flight mass spectrometer analyzes the product ions according to their masses and yields.
With this setup trace gas compounds can be measured in a concentration range from several ppmv down to the ppqv (parts-per-quadrillion) region [4] with a typical response time well below 100ms and, in case a TOF mass analyzer is used, a mass resolution better than 6.000 m/Δm. One can easily see that these performance data would make the PTR-MS technology an ideal candidate for the detection of illicit substances such as explosives, CWAs, drugs.
Here we present first results of measurements on explosives and a chemical warfare (CWA) analogue utilizing a high mass resolution and high sensitivity PTR-TOF-MS instrument as well as a quadrupole based PTR-MS instrument. In addition we present data obtained with our novel "inlet booster system", which improves the detection limit by a factor of 500 already in its preliminary version.

Inlet booster system

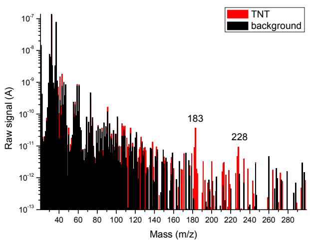
The sample air is drawn through a metal mesh at a high flow rate for about 10s. Afterwards the mesh is resistively heated and the evaporating compounds are analyzed with a common PTR-MS instrument. The whole process takes less than one minute and can therefore still be called "online".



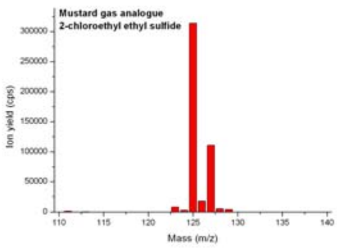
Direct inlet



Direct inlet measurement on a high mass resolution time-of-flight (PTR-TOF-MS) instrument. TNT on protonated mass 228.025m/z can be clearly separated from an unknown lab-air compound.

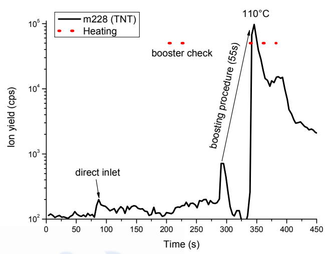


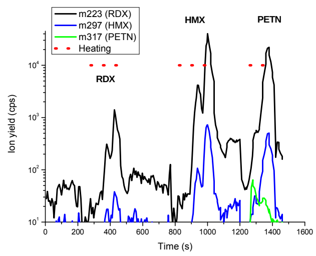
Mass spectrum of TNT utilizing a Compact PTR-Quad-MS (reduced in size and weight but also in sensitivity). The protonated parent ion on mass 228m/z can still be detected. On mass 183m/z we observe protonated DNT, which is a known impurity of commercial TNT and has a significantly higher vapor pressure.



Part of a mass spectrum obtained with a PTR-Quad-MS of a vial that was flushed with C_4H_9ClS (compare: mustard gas $C_4H_8Cl_2S$). Note the extremely high signal intensity and the nicely matching isotope ratio between mass 125 and 127m/z that makes an unambiguous identification possible.

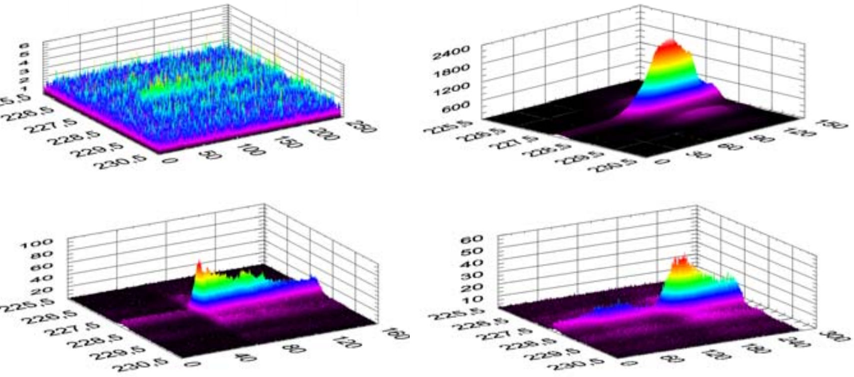
Inlet booster





Performance check of the inlet booster system (PTR-Quad-MS). The left diagram shows a measurement on TNT, at first via the direct inlet (~200cps), then a check if the booster is clean and finally a 55s boosting procedure that leads to an increase in signal intensity by a factor of ~500. The right diagram demonstrates that the principle also works for other explosives (Note: the booster was not cleaned between the three samples).

Tests on a few mg of TNT in a glass vial utilizing a PTR-TOF-MS. Top left: direct inlet starting at about cycle 50; top right: utilizing the inlet booster system on open vial; bottom left: utilizing inlet booster system on closed vial; bottom right: utilizing inlet booster system on human finger that was in contact with TNT (first ~100 cycles: check if booster is clean).



Acknowledgement
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References
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[2] J. de Gouw, C. Warneke, T. Karl, G. Eerdekens, C. van der Veen, R. Fall; Mass Spectrometry Reviews, 26 (2007), 223-257.
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[4] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer and T.D. Märk, Int.J.Mass Spectrom., 286 (2009) 32-38.