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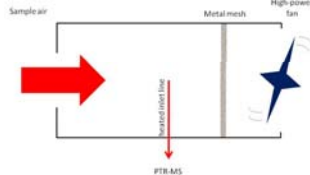
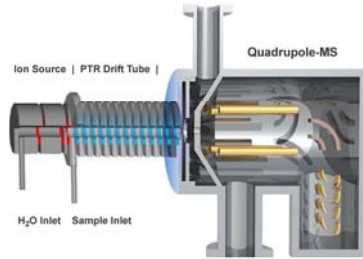
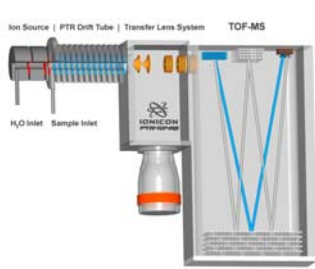
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Abstract

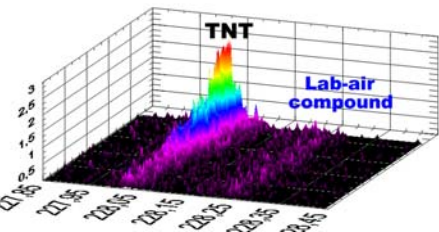
Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is an innovative technology invented and developed by scientists of the "Institut für Ionenphysik" at the Leopold-Franzens University in Innsbruck and made commercially available by the spin-off company IONICON Analytik GmbH. Details about the technique have been described elsewhere (e.g. [1], [2] and very recently [3]). In short, in a hollow cathode ion source hydronium ions (in the newest mode also NO⁺ or O₂⁺) 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 O₂⁺) 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 5.000 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.

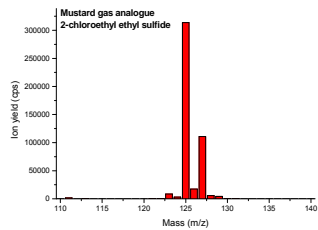
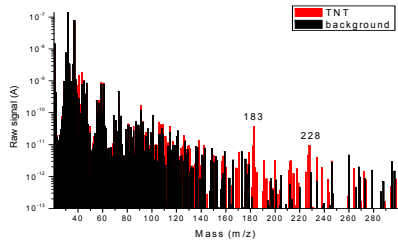


Inlet booster system
The sample air is drawn through a metal mesh at a high flow rate for about 10s. Afterwards the mesh is resistively heated and the evaporating compounds are analyzed with a common PTR-MS instrument. The whole process takes less than one minute and can therefore still be called "online".

Direct inlet

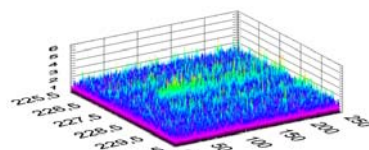


Direct inlet measurement on a high mass resolution time-of-flight (PTR-TOF-MS) instrument. TNT on protonated mass 228.025m/z can be clearly separated from an unknown lab-air compound.

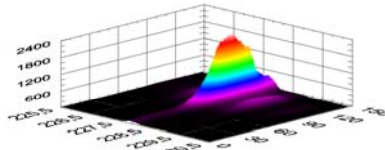


CWA
Part of a mass spectrum obtained with a PTR-Quad-MS of a vial that was flushed with C₄H₉ClS (compare: mustard gas C₄H₈Cl₂S). Note the extremely high signal intensity and the nicely matching isotope ratio between mass 125 and 127m/z that makes an unambiguous identification possible.

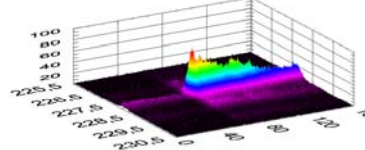
Tests on a few mg of TNT in a glass vial utilizing a PTR-TOF-MS



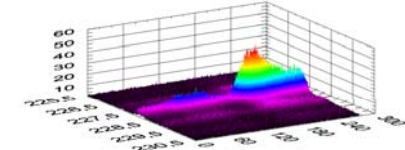
direct inlet starting at about cycle 50



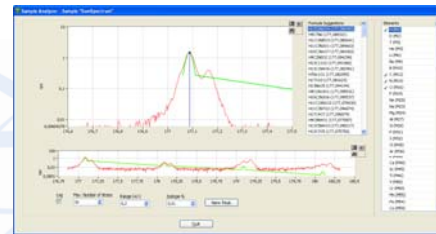
utilizing the inlet booster system on open vial



utilizing inlet booster system on closed vial



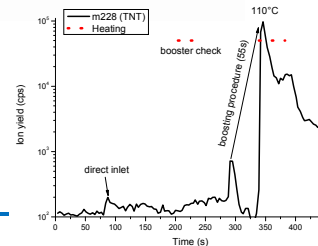
utilizing inlet booster system on human finger that was in contact with TNT (first ~100 cycles: check if booster is clean)



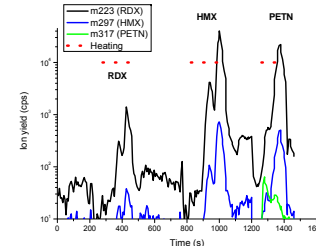
Software

To demonstrate both, the extreme mass accuracy of the PTR-TOF-MS and the high degree of development of IONICON's data analysis software, the figure on the left shows a part of a mass spectrum obtained from the plastic explosive Semtex. DMNB is a marker commonly used in explosives with the exact protonated mass 177.0875amu. In the spectrum this substance is detected at 177.087m/z and automatically identified as C₆H₁₃N₂O₄. The correctness of this automatic identification can be checked e.g. via the distribution of isotopes in the lower part of the window.

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 works also for other explosives (Note: the booster was not cleaned between the three samples).



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.

References

- [1] W. Lindinger, A. Hanel, A. Jordan; Int. J. of Mass Spectrom. and Ion Processes, 173/3 (1998) 191-241.
- [2] J. de Gouw, C. Warneke, T. Karl, G. Eerdeken, C. van der Veen, R. Fall; Mass Spectrometry Reviews, 26 (2007), 223-257.
- [3] R. S. Blake, P. S. Monks, A. M. Ellis; Chem. Rev., 109 (3) (2009), 861-896.
- [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.