

Proton-Transfer-Reaction Time of Flight Mass-Spectrometry (PTR-TOF-MS): Comparison of Compact-Time of Flight (C TOF) and High Resolution-Time of Flight (HRS TOF) Platforms

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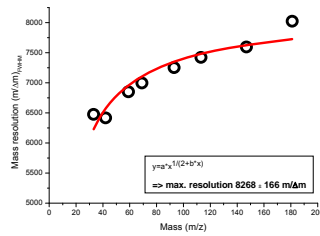
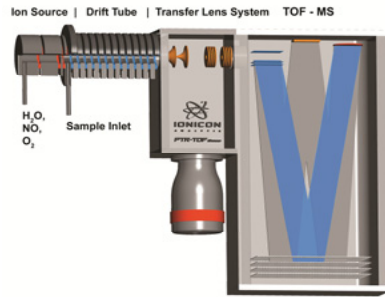
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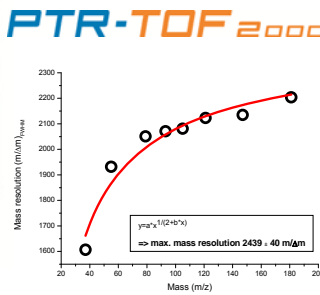
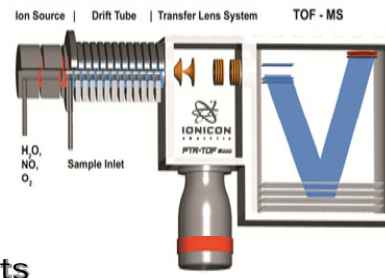
Abstract

Here we present IONICON's latest developments in PTR-TOFMS technology which exceed previously reported TOF setups [1-3] in terms of high sensitivity, low detection limit and fast response time [4]. We demonstrate the great potential of these newly developed instruments in various fields of application, ranging from measurements of air samples to the detection of illicit substances.

Combining a time-of-flight (TOF) mass spectrometer with the established PTR technology offers a variety of advantages compared to quadrupole mass filter based instruments: In contrast to PTR-QMS instruments, the high mass resolution HRS PTR-TOF-MS (commercially available as PTR-TOF 8000) can generate entire mass spectra (snapshots) of complex trace gas mixtures in split-seconds with an outstanding mass resolution (in V-mode > 8000 m/Δm) and with virtually no upper mass limit. Comparison measurements with a C PTR-TOF-MS (commercially available as PTR-TOF 2000) showed an increase of sensitivity at a somewhat lower mass resolution (> 2000 m/Δm).



PTR-TOF 8000



PTR-TOF 2000

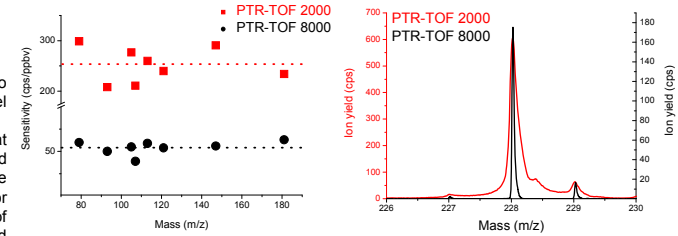
Performance of the setup

A calibration gas standard mixture was used to determine the performance of the two novel instruments.

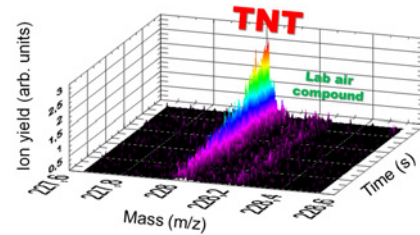
On the left the mass resolution (full width at half maximum, FWHM) for every compound was calculated. It can easily be seen that the resolution increases with higher masses for both instruments and reaches a maximum of over 8.000 m/Δm for the PTR-TOF 8000 and over 2.000 m/Δm for the PTR-TOF 2000. It is noteworthy that although the PTR-TOF 8000 can be used in W-mode, the present measurements were performed in V-mode, i.e. an even high resolution would be possible at the cost of lower sensitivity.

With the same gas standard the sensitivities of both instruments were determined. On the top right figure it can be seen that the sensitivity of the PTR-TOF 2000 is about five times the sensitivity of the PTR-TOF 8000.

In the very right figure both performance features are demonstrated on behalf of a "real-life" measurement, namely the headspace above a small quantity of trinitrotoluene (TNT). The measurement was done by connecting both instrument's inlet lines with a T-piece, i.e. the results are directly comparable.



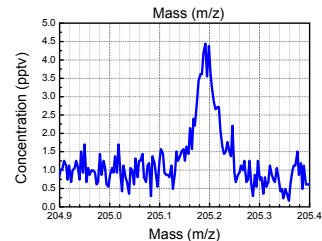
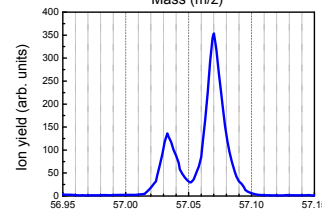
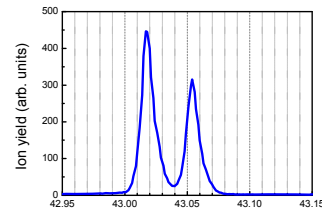
On the right a 3D figure of a measurement on TNT is shown. Coincidentally a (unknown) compound was present on the same nominal mass as TNT during this measurement in the lab air. It can be seen that while approaching the TNT sample with the inlet tube, the signal on the exact mass of TNT increases while the signal for the harmless lab air compound stays constant.



Results

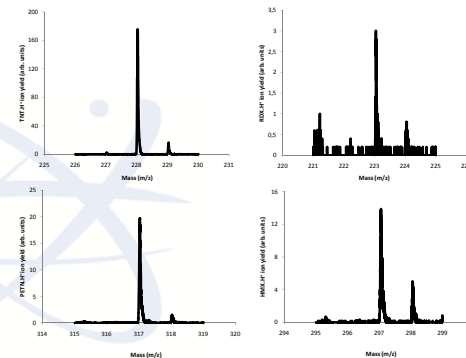
In practical applications the high mass resolution of the PTR-TOF 8000 makes it e.g. possible to separate isobaric compounds out of an urban air sample: While the top left graph shows the mass separation of protonated ketene (first peak, 43.018 m/z) and propene (second peak, 43.055 m/z), the middle diagram displays the separation of protonated methylketene (first peak, 57.034 m/z) and butene (second peak, 57.070 m/z). Based on these measurements we can conclude that the extraordinary mass resolution of the novel instrument makes the identification of substances much easier and more unambiguous than for quadrupole instruments.

Sesquiterpenes are present in extremely low concentrations in urban air samples and are therefore very well suited to demonstrate the outstanding detection limit of the PTR-TOF 8000. In the bottom figure sesquiterpene at 205.196 m/z is present at a concentration level of about 4 pptv and can still be clearly separated from the instrument's background noise.



Common solid explosives are very difficult to detect in the gas phase because of their extremely low vapor pressures.

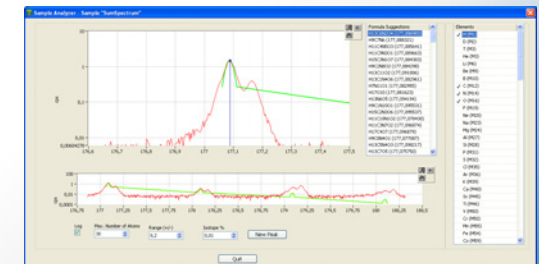
In the graphs on the right we investigated the headspace of four of the most common explosives, namely TNT (top left), RDX (top right), PETN (bottom left) and HMX (bottom right). All measurements were performed at room temperature and with the standard inlet system of PTR-TOFMS instruments. Besides the remarkable fact that all four explosives could be clearly detected, the results also show that PTR-TOFMS can be used for substance identification on a very high accuracy level, i.e. by combining the information on the exact mass with the isotope ratio the probability for "false positives" gets negligible [5,6].



Software

To demonstrate both, the extreme mass accuracy of the PTR-TOF 8000 and the high degree of development of IONICON's data analysis software, the figure below 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 177.0875 amu. In the spectrum this substance is detected at 177.087 m/z and automatically identified as C₈H₁₃N₂O₄. The correctness of this automatic identification can be checked e.g. via the distribution of isotopes in the lower part of the window.



Acknowledgement

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