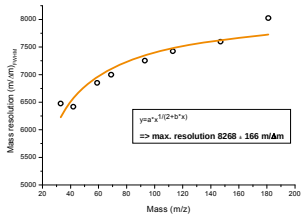
More than one order of magnitude higher sensitivities with Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOFMS)

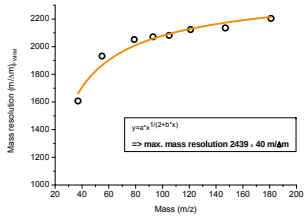
Lukas Märk[1], Alfons Jordan[1], Christian Lindinger[1], Eugen Hartungen[1], Achim Edtbauer[1], Simone Jürschik[1], Philipp Sulzer[1], Tilmann D. Märk[1,2]

[1] *IONICON Analytik GmbH, Eduard-Bodem-Gasse 3, 6020 Innsbruck, Austria*
[2] *Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria*

Abstract

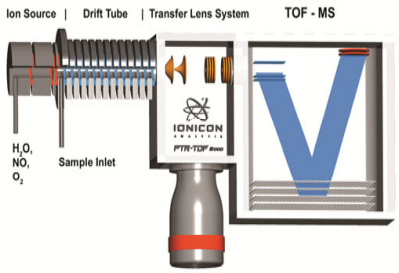
In 2009 we published a paper on the development of a high resolution and high sensitivity **Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOFMS)** instrument [1]. Although the coupling of a PTR source to a TOF mass analyzer had already been reported by other groups at that time, our development had an outstanding impact in the PTR-MS community as for the first time a mass resolution of about 7000 m/Δm and a sensitivity of up to 25 cps/ppbv was achieved. This novel **instrumentation revolutionized direct-injection mass spectrometry** in ample fields of application (**environmental research, food and flavor analysis, health sciences, etc.**) [2].
Here we report on a number of instrumental developments, leading to serious **improvements in sensitivity and in the detection limit**, while keeping the **mass resolution outstandingly high**. We present measurements on gas standards illustrating the advances in instrumental development.





Mass dependent resolution curves including appropriate fitting functions for the determination of the **maximum resolution**.

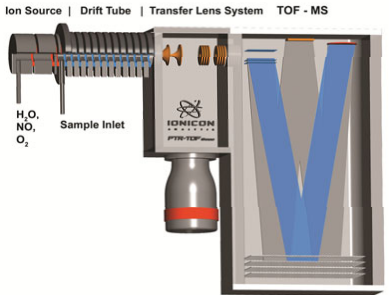
Top: PTR-TOF 8000
Bottom: PTR-TOF 2000



PTR-TOF 2000

Experimental Setup

A typical PTR-TOFMS instrument consists of an ion source, where water vapor is converted into H_3O^+ in a hollow cathode discharge and an adjacent drift tube, where the actual proton transfer to the trace gas compounds takes place. The protonated product ions are finally analyzed and detected in a TOF mass spectrometer. It is obvious that for such an instrument a virtually countless number of parameters contribute to the overall performance (instrumental design, lens voltages, orifice diameters, differential pressures, etc.). We consecutively **improved and optimized these parameters**, which in sum contribute to an increase in instrumental performance of over one order of magnitude without any decrease in mass resolution.
The schematic illustration on the left represents the setup of a so-called "PTR-TOF 2000", i.e. a TOF based PTR-MS instrument with an increased sensitivity. On the right the schematic for a "PTR-TOF 8000", which performs at an increased mass resolution is displayed.



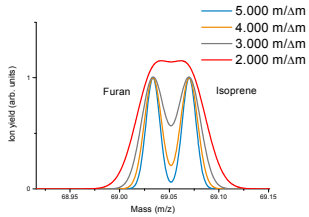
PTR-TOF 8000

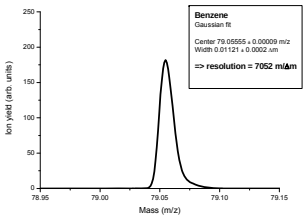
Compound	Molecular composition	Protonated mass (*m/z*)
Benzene	C_6H_6	79.054
Toluene	C_7H_8	93.070
Styrene	C_8H_8	105.070
Ethylbenzene	C_8H_{10}	107.086
Xylene	C_8H_{10}	107.086
Chlorobenzene	C_6H_5Cl	113.015
Trimethylbenzene	C_9H_{12}	121.101
Dichlorobenzene	$C_6H_4Cl_2$	146.976
Trichlorobenzene	$C_6H_3Cl_3$	180.937

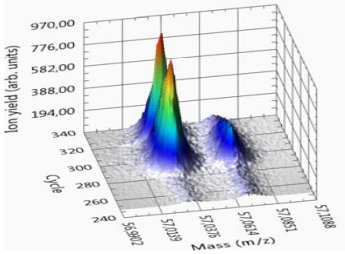
List of compounds in the gas standard used for the determination of sensitivities and LoDs.

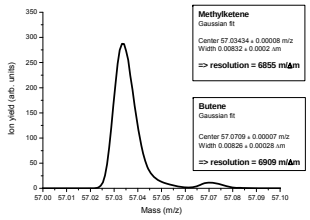
Top: calculated peak shapes for different mass resolutions for two isobaric substances present at the same intensity.

Bottom: actual measurement performed with a PTR-TOF 8000 on benzene; a Gaussian fit shows a resolution of over 7000 m/Δm.









Measurement data obtained from samples containing methylketene and butene to illustrate the importance of **high resolution** for isobars separation.

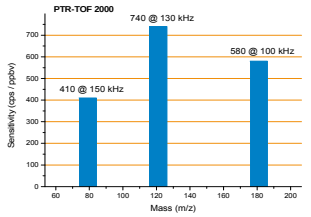
Top: 3D view to demonstrate the time evolution of the independent intensities.

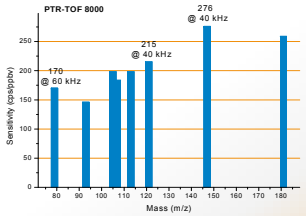
Bottom: Average over a defined amount of cycles in order to determine the exact peak positions and the mass resolution.

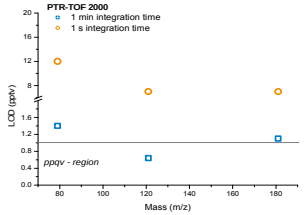
Results of the **sensitivity** determination utilizing the gas standard shown in the top left table. Values are stated in cps/ppbv at the corresponding TOF extraction rate.

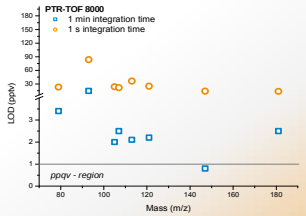
Top: PTR-TOF 2000; maximum sensitivity is about **750 cps/ppbv**.

Bottom: PTR-TOF 8000; maximum sensitivity is about **300 cps/ppbv**.









Results of the **LoD** determination utilizing the gas standard shown in the top left table. The LoDs were calculated using the common 3σ (standard derivation) method.

Top: PTR-TOF 2000; limits of detection are **0.6 - 1.5 pptv.**

Bottom: PTR-TOF 8000; limits of detection are **0.8 - 3 pptv.**

References
[1] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer, T.D. Märk, Int. J. of Mass Spec., 286 (2009), 122–128.
[2] F. Biasioli, C. Yeretzian, T. D. Märk, J. Dewulf, H. Van Langenhove, Trends in Analytical Chemistry 30 (7) (2011).