

Novel Developments in Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS): Switchable Reagent Ions (PTR+SRI-MS) and ppqv Detection Limit

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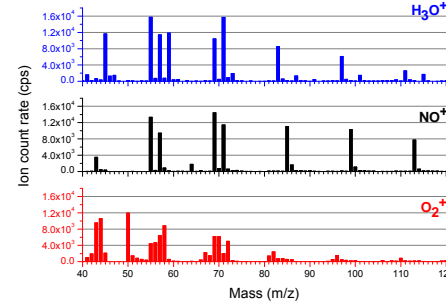
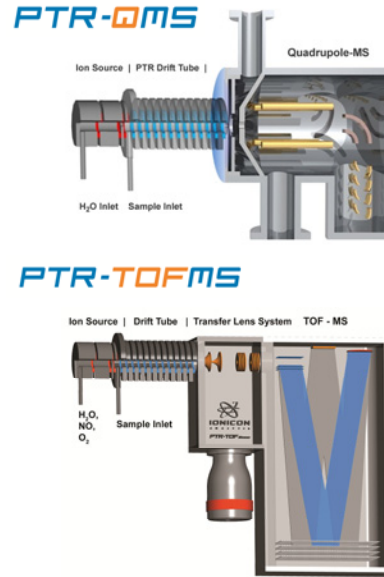
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Abstract

Since many years Proton Transfer Reaction - Mass Spectrometry (PTR-MS) is a well established technique for real-time trace gas analysis (for details see [1] and very recently [2]). In short, in a hollow cathode ion source reagent ions 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. Finally either a quadrupole or a time-of-flight mass spectrometer analyzes the product ions according to their masses and yields.

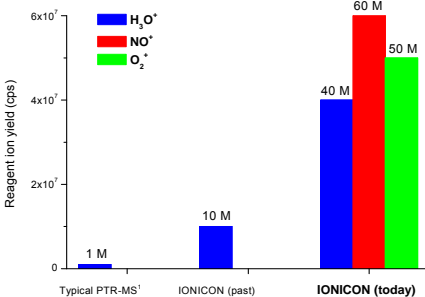
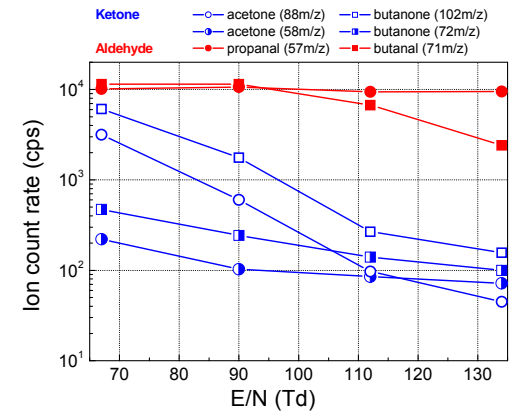
Here we report on the latest instrumental developments [3], namely i) the improvement of the detection limit that now allows for measuring trace gas compounds in a concentration range from several ppmv down to the ppqv (parts-per-quadrillion) region with a typical response time well below 100ms and, in case a TOF mass analyzer is used, a mass resolution up to 8.000m/Δm and ii) the possibility to switch between H₃O⁺, NO⁺ and O₂⁺ as reagent ions. We show, that the sensitivities obtained with NO⁺ and O₂⁺ are comparable to the outstanding sensitivity of the established PTR-MS instruments and therefore well above those from e.g. IMR-MS or SIFT-MS instruments.



The diagrams above show a comparison of mass spectra obtained from 8 aldehydes using H₃O⁺, NO⁺ and O₂⁺. It can be easily seen that NO⁺ leads to the simplest spectrum mainly giving dehydrogenated cations (M-H)⁺. O₂⁺ on the other hand reacts via exothermic charge transfer resulting in stronger fragmentation, whereas proton transfer from H₃O⁺ produces mostly protonated parent molecules (MH⁺). In conclusion the combination of all three mass spectra dramatically improves the identification capability of PTR-MS instruments.

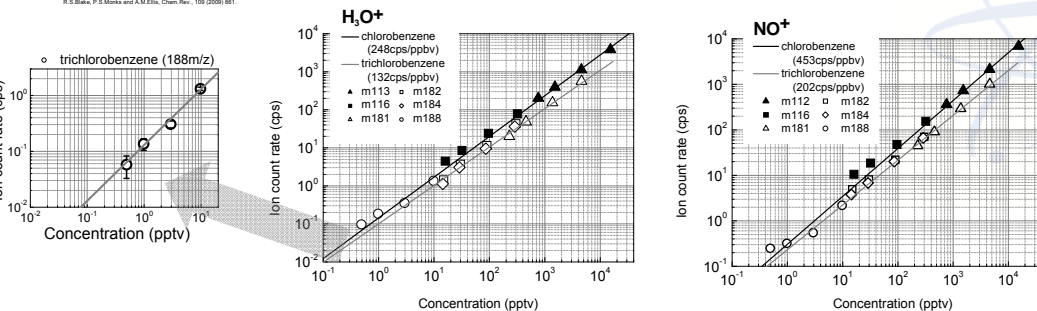
NO⁺

With NO⁺ as reagent ions it is possible to distinguish between several isomers: According to [4] reactions with aldehydes yield in dehydrogenated product ions, whereas reactions with ketones produce intact products and clusters. In the figure below this behavior is demonstrated on behalf of two isomeric pairs in dependence of the collision energy.



High sensitivity / low detection limit

The changes in the PTR setup not only open the possibility to switch between different reagent ions, but also improve the overall sensitivity of the system. One of the main factors influencing the instrument's sensitivity is the intensity of the primary ion current. In the bargraph on the left a comparison of primary ion intensities is shown (one example out of [2], Ionicon PTR-MS a few years ago, actual study [3]). Furthermore the two correlation plots below display the concentration in pptv vs. the product ion count-rate in cps (for H₃O⁺ the small diagram shows the trichlorobenzene data close to the detection threshold after subtraction of the background signal).



O₂⁺

In the table above two examples for molecules that cannot be ionized with PTR are given. However, by using O₂⁺ as reagent ions these two important everyday-life substances undergo charge transfer ionization and can therefore be analyzed with the outstanding sensitivity of a PTR-QMS or the high sensitivity and mass resolution of a PTR-TOFMS.

	H ₃ O ⁺	O ₂ ⁺
	166.5 kcal/mol	12.1 eV
Ethylene (C ₂ H ₄)	162.5 kcal/mol	10.5 eV
Acetylene (C ₂ H ₂)	153.2 kcal/mol	11.4 eV
	no	yes

References

- [1] W. Lindinger, A. Hansel, A. Jordan, Int. J. of Mass Spectrom. and Ion Processes, 173/3 (1998) 191-241.
- [2] R. S. Blake, P. S. Monks, A. M. Ellis, Chem. Rev., 109 (3) (2009), 861-896.
- [3] 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.
- [4] P. Spanel, Y. Ji, D. Smith, Int. J. of Mass Spectrom. and Ion Processes, 165/166 (1997) 25-37.