A FastGC Proton-Transfer-Reaction Quadrupole Ion Guide Time-of-Flight (PTR-QiTOF) Mass Spectrometer

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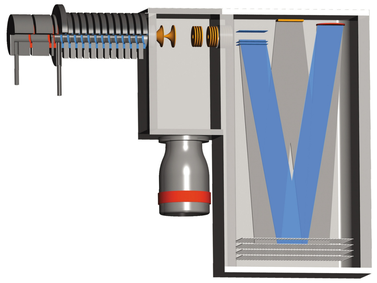
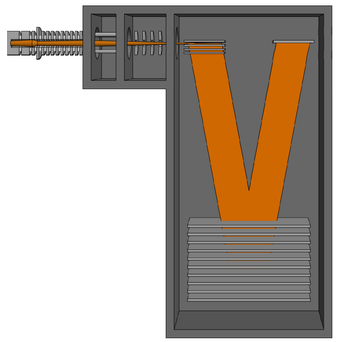
Abstract

High sensitivity, low **limit-of-detection (LoD)**, short **response time** in the **100 ms** regime and **direct injection** without sample preparation have made **Proton-Transfer-Reaction - Mass Spectrometry (PTR-MS)** a well-established technology in **environmental sciences, food and flavor research, etc.** [1]. As in these fields often **isomeric compounds** have to be i**dentified** and **quantified independently**, there is a need **for additional methods** to **increase selectivity**.
In the past traditional Gas Chromatography (GC) has been coupled with PTR-MS instruments [2], which at that time were based on quadrupole mass filters and thus only provided information about the nominal masses of product ions. However, this combination lacks the ability for **real-time analysis**, which is one of the major advances of PTR-MS.
Here we introduce a novel approach where we integrate a **fast GC column ("fastGC")** into a **PTR-QiTOF instrument.** The outstanding sensitivity of the new PTR-QiTOF (up to 4,700 cps/ppbv; [3]) is crucial for applications where time per analysis is limited, e.g. nosespace in food and flavor research. Particularly, in these fields the chemical environment is normally very complex so that a high selectivity is essential as well. Consequently with this novel setup we combine the advantages of both technologies to a very powerful tool: **high selectivity and high sensitivity in near-real-time.**
We present first results of **monoterpene measurements**, which are very dominant compounds in atmospheric chemistry as well as in food and flavor research.



PTR-TOF 8000



PTR-QiTOF

Performance Comparison

The **figures to the left** show schematics of the two compared instruments: the **well-established** [5] **PTR-TOF 8000** and the **innovative PTR-QiTOF** with its **extreme high sensitivity** and **high mass resolution.**
Both instruments have a hollow cathode ion source as a core piece which produces reagent ions at a very high purity level (up to 99.5%). After ion generation they are introduced into the adjacent drift tube **without** the need of a **mass filter** where different chemical ionization processes take place. This ionization soft, yielding **low fragmentation** and is very efficient, permitting **real-time quantification** and extremely **low detection limits.**
In case of the **PTR-TOF 8000** a common transfer **lens system** is placed between the drift tube and the mass spectrometer, whereas the **PTR-QiTOF** utilizes a **quadrupole ion guide.** Finally, a **time-of-flight mass spectrometer** analyzes the product ions according to their masses and yields.

In the **figures to the right** comparisons of the two instruments are presented utilizing **certified gas standards**: **sensitivities** at different masses, **mass resolving power** (for trichlorobenzene), **linearity** from about 100 ppbv down to the respective LoDs (dichlorobenzene isotopes; 10s integration time). The high sensitivity / low LoD makes the **PTR-QiTOF** an ideal tool for applications where analysis time is limited (e.g. flux measurements).

Acknowledgement
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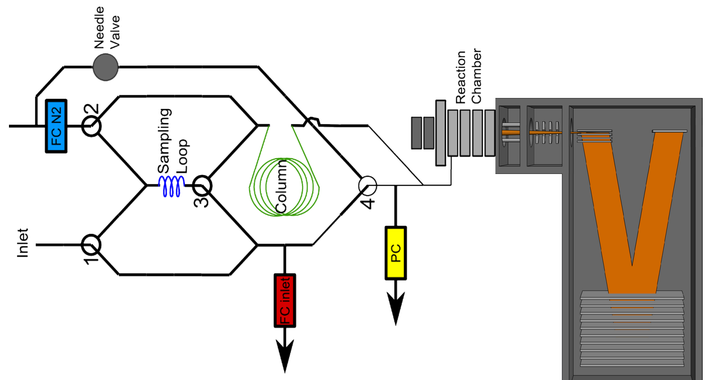
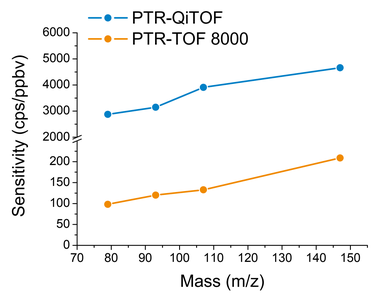
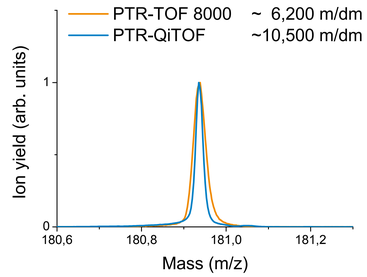
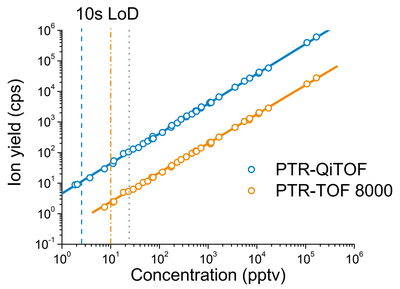




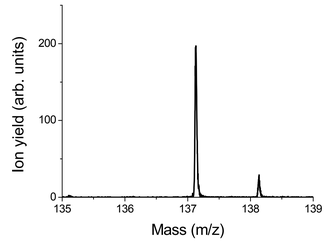




PTR-MS + fastGC

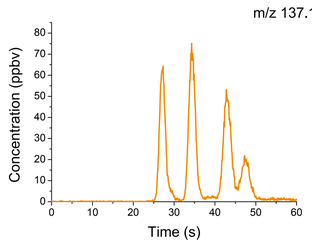
The **figure to the left** shows a schematic view of the integrated **fastGC setup**. In this case the fastGC is installed inside a PTR-QiTOF instrument. Via electronically controlled valves the PTR-MS inlet system can be switched between **direct injection and fastGC mode [4]**.
In **direct injection mode** (fastGC disabled) the system operates as a **normal PTR-MS instrument**, i.e. with **continuous sampling**, response times in the 100 ms regime and real-time quantification. When the instrument is switched to **fastGC mode**, a **sample loop** gets **filled** with **the sampling gas** entering the instrument's inlet line. Then the **content** of the sample loop **is injected into** the **fastGC column** and the compounds enter the drift tube of the PTR-MS instrument, temporally **separated according** to their **retention times**. Since temperature is the crucial factor influencing the separation efficiency of the column, a heating ramp can be configured to optimize the passage of substances with large retention times. Fast heating and cooling rates of the fastGC allow a **spectral run** of **less than one minute**.

The figure below shows a typical **mass spectrum** for a **monoterpenes**-mixture ionized with H_3O^+ (around the protonated *m/z* 137). Even with a high-resolution mass spectrometer the isomers cannot be separated. By **switching** the PTR-TOFMS instrument **to fastGC mode**, the different **monoterpenes get separated** in **less** than **60s** and can be quantified independently (**orange** and **blue** figure below for *m/z* 137 in **spruce resin** and **manuka tea**, respectively).
The grey diagram in the middle shows a FastGC measurement on an α-pinene standard which proves nicely that for manuka tea α-pinene is by far the most abundant monoterpene.

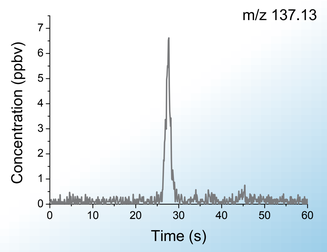


FAST GC

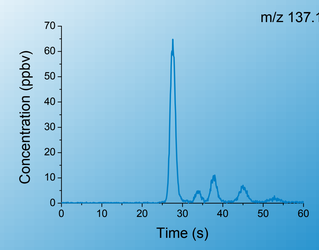
Spruce resin



Pinene standard



Manuka tea



References

[1] A.M. Ellis, C.A. Mayhew, In: Proton Transfer Reaction Mass Spectrometry: Principles and Applications, Chichester, UK: John Wiley & Sons, Ltd (2014).
[2] C. Lindinger, P. Pollien, S. Ali, C. Yeretzian, I. Blank, T.D. Märk, Anal. Chem. 77(13) (2005) 4117..
[3] P. Sulzer, E. Hartungen, G. Hanel, S. Feil, K. Winkler, P. Mutschlechner, S. Haidacher, R. Schottkowsky, D. Gunsch, H. Seehauser, M. Striednig, S. Jürschik, K. Breiev, M. Lanza, J. Herbig, L. Märk, T.D. Märk, A. Jordan , Int. J. Mass Spectrom 368 (2014), 1-5.
[4] V. Ruzsanyia, L. Fischer, J. Herbig, C. Ager, A. Amann, J. of Chromatography A 1316 (2013) 112.
[5] P. Sulzer, S. Jürschik, B. Agarwal, T. Kassebacher, E. Hartungen, A. Edtbauer, F. Petersson, J. Warmer, G. Holl, D. Perry, K. Becker, C. A. Mayhew, T. D. Märk, CCIs 318 (2012) 366.