

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

Alfons Jordan¹, Lukas Märk¹, Jens Herbig¹, Christian Lindinger¹, Rene Gutmann¹, Lukas Fischer¹, Eugen Hartungen¹, Simone Jürschik¹, Gernot Hanel¹, Philipp Sulzer¹, 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

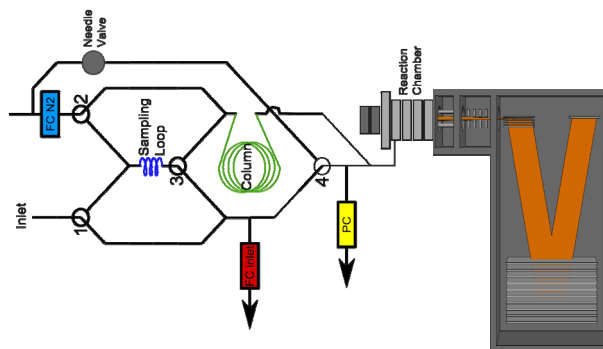
Abstract

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 **identified 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.



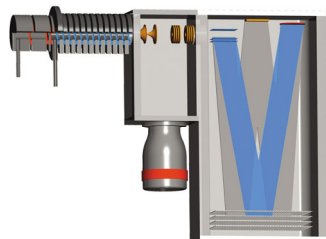
PTR-MS + fastGC

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].

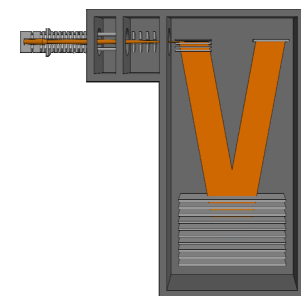
In **direct injection mode** (fastGC disabled) the system operates as a **normal PTR-MS instrument**, i.e. with **continuous sampling**, response times in the 100 ms regime and real-time quantification. When the instrument is switched to **fastGC mode**, a **sample loop** gets filled with the **sampling 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, temporarily **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.



PTR-TOF 8000



PTR-QiTOF

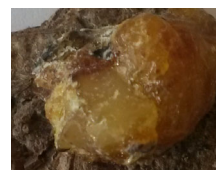
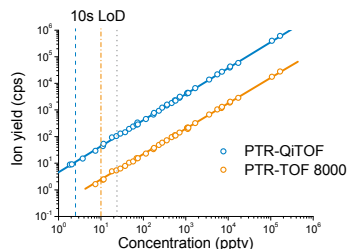
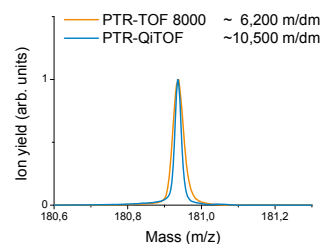
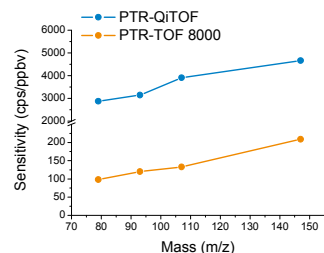
Performance Comparison

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**.

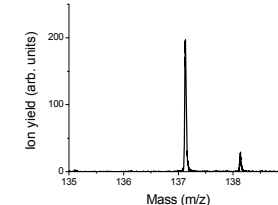
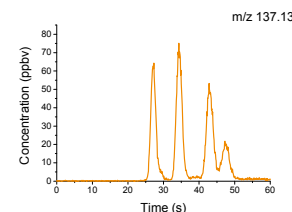
Both instruments have a hollow cathode ion source as a core piece which produces reagent ions at a very high purity level (up to 99.5%). After ion generation they are introduced into the adjacent drift tube **without the need of a mass filter** where different chemical ionization processes take place. 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.

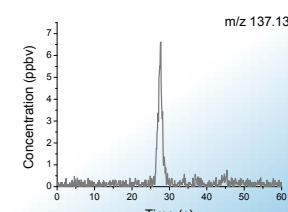
In the **figures to the right** comparisons of the two instruments are presented utilizing **certified gas standards: sensitivities** at different masses, **mass resolving power** (for trichlorobenzene), **linearity** from about 100 ppbv down to the respective LoDs (dichlorobenzene isotopes; 10s integration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



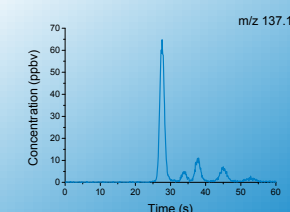
Spruce resin



Pinene standard



Manuka tea



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