Recent Advances in Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

Marc Gibert[1], Philipp Sulzer[2], Simone Jürschik[2,3], Alfons Jordan[2], Gernot Hanel[2], Eugen Hartungen[2] and Tilmann D. Märk[2,3]

[1] Ingenieria Analítica S.L., Avda. Cerdanyola 73 - 08172 Sant Cugat del Valles Barcelona, Spain

[2] IONICON Analytik GmbH, Eduard-Bodem-Gasse 3, 6020 Innsbruck, Austria

[3] Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria

The innovative Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) technology was invented and developed in the 1990s by scientists of the "Institut für Ionenphysik" at the Leopold-Franzens Universität in Innsbruck and was commercialized by the spin-off company IONICON Analytik GmbH. PTR-MS rapidly became a well established analytical technology [1] in the fields of environmental research, atmospheric chemistry, and food and flavor science. This resulted from its high selectivity, extremely low detection limits, rapid response times and real-time quantification capability.

The technology has been described in much detail in various publications. In short, a hollow cathode ion source produces H_3O^+ ions from distilled water at extremely high purity levels (over 99%), i.e. no mass filter is needed after the ion source to purify the primary ions. Subsequently the hydronium enters a drift tube where the trace compounds get ionized via proton transfer and finally analyzed with either a quadrupole mass filter or a time-of-flight (TOF) mass analyzer.

Here we report on the latest instrumental developments, 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 100 ms, (ii) the coupling of our sophisticated PTR source to two different types of time-of-flight (TOF) mass analyzers (one with an outstanding mass resolution called PTR-TOF 8000 [2] and one with an increased sensitivity called PTR-TOF 2000 [3]) and (iii) the possibility to switch between H_3O^+, NO^+ and O_2^+ as reagent ions [4].

Development (i) allows us to enter new fields of application where extremely high sensitivities are needed. Explosives for example possess extremely low vapor pressures and are therefore difficult to detect in the gas phase. We performed proof-of-principle measurements where we could detect and identify common solid explosives by analyzing the headspace above small quantities of samples at room temperature and also from trace quantities not visible to the naked eye placed on surfaces.

The use of TOF detectors in (ii) is especially important for applications where not only high sensitivity but also unambiguous identification is needed (e.g. detection of chemical warfare agents [5]). The high mass resolution of up to 8.000 m/Δm and accuracy of the PTR-TOF 8000 allow for separation of most isobaric compounds and for substance identification via the exact mass. As there might be applications where an enormous mass resolution is not necessarily needed, but the sensitivity has to be as high as possible, the PTR-TOF 2000 performs with an enhanced sensitivity at the expense of a somewhat lower mass resolution. We present comparison data which demonstrate that the resolution of this PTR-TOF 2000 is still around 2.000 m/Δm while showing an increased sensitivity by a factor of five compared to the PTR-TOF 8000.

For iii) we show, that the sensitivities obtained with NO^+ and O_2^+ are comparable or even better than the outstanding sensitivity of the established PTR-MS instruments and therefore well above those from e.g. SIFT-MS instruments. To demonstrate the advantages of this so called "SRI" (switchable reagent ions) setup we e.g. measured acetone and propanal (isomeric molecules at nominal mass 58 amu) utilizing NO^+ as the precursor ion. According to Spanel et al. [6] NO^+ interactions with aldehydes follow the reaction: $NO^+ + XH \rightarrow X^+ + NOH$ whereas ketones follow: $NO^+ + XH \rightarrow XH^+ + NO$ (and clustering). This means that we see isomeric compounds on different nominal masses and can identify them unambiguously. Furthermore, by using O_2^+ precursor ions we are able to ionize molecules via charge transfer reactions that cannot be measured via hydronium proton transfer reaction.

References:

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