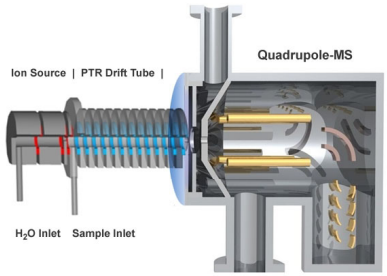
Monitoring and Quantifying Toxic Industrial Compounds (TICs) with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

A. Jordan[1], C. Lindinger[1], L. Märk[1], P. Sulzer[1], S. Jürschik [1], H. Seehauser[1], T.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

Proton-transfer-reaction mass spectrometry (PTR-MS) is a powerful technology because of its wide spectrum of advantages, e.g. high sensitivity, low detection limit and fast response time. Therefore this technology is already well established in the fields of **food and flavor science** [1], **environmental and biological research** [2], **medicine and biotechnology, etc.**
In contrast to chemical warfare agents (CWAs) which are very hard to get hold of by terrorists, **toxic industrial compounds (TICs)** are part of our everyday lives. Thousands of tons of TICs are used in chemical industry worldwide and can **endanger human life** either when **accidentally released** from factories or when **misused as a weapon** in terrorist attacks. Thus there is a need for a fast, sensitive and reliable method for the real-time detection and quantification of these compounds.
Here we present (unpublished) results on our latest PTR-MS studies on different TICs. This study complements our previous work on the detection of explosives [3], CWAs [4] and illicit and prescribed drugs [5] and introduce PTR-MS as an universal detector for an ample number of potentially dangerous substances.



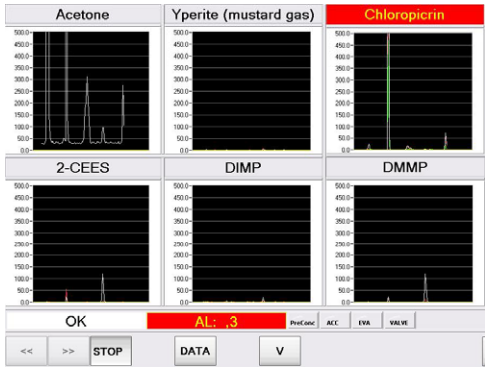
top
Schematic of a PTR-QMS illustrating the main components of a PTR-MS instrument

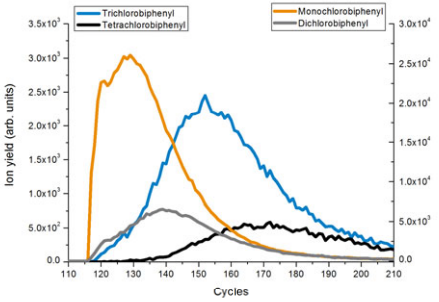
left
Picture of a PTR-QMS especially constructed for compound monitoring (approx. a 55 cm / 22 in. cube).

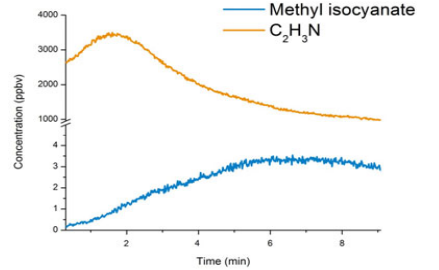
PTR-MS technology

In a hollow cathode ion source hydronium (H_3O^+) is produced from water vapor at purity levels of >99%. Without the need of a mass filter the H_3O ions are introduced into the adjacent drift tube where the proton transfer to all molecules that possess a lower proton affinity than water takes place. This ionization process is very soft (**low fragmentation**) and efficient, thus permitting **real-time quantification** and extremely **low detection limits**.
Depending on the envisaged field of application the PTR part can be coupled either to a **time-of-flight (TOF)** or to a **quadrupole** mass spectrometer **(QMS)**. The PTR-TOF version allows for the separation of many isobaric compounds because of the high mass resolution (e.g. up to **8 000 m/Δm** for a PTR-TOF 8000 [6]), whereas the PTR-QMS is ideal for monitoring specific substances down to very low concentrations (**below pptv** level [7]) while keeping the overall dimensions of the instrument very compact.

bottom
Screenshot of a specialized detection software based on the scientific results of the present study. In the picture six substances are monitored simultaneously and identified via their protonated masses and fragments / isotopes. As soon as a preset threshold is exceeded an alarm is triggered (red color).



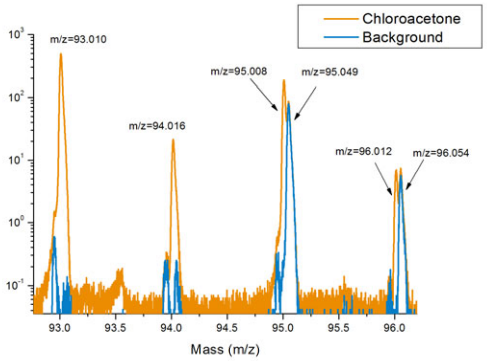




left
The upper figure on the left side shows an analysis of the highly carcinogenic environmental pollutants **polychlorinated biphenyls (PCBs)** using a PTR-QMS instrument. A standard mixture of the indicated PCBs was placed into a vial and subsequently heated. In order of their volatility the increase and decrease of the ion yields for the different PCBs can be monitored.
The lower figure shows a measurement of the highly toxic substance **methyl isocyanate (MIC)**, which was e.g. released in a chemical accident in India in the 1980s and caused death of several thousand people. The MIC we used was present in trace amounts bound to polystyrene, from which some mg were put in a vial. It can be seen that at the beginning of the measurement virtually no MIC is present in the headspace. During the following minutes we heated the sample to approximately 100°C. The release of MIC from the polystyrene can be monitored in real-time during the temperature rise. However, at the same time we recognized that our sample also contained contaminations at rather high concentrations. Due to the high mass resolution of the PTR-TOF 8000 used we could identify e.g. the peak at nominal mass 42 m/z as protonated C_2H_3N (most probably acetonitrile). Although the concentration of C_2H_3N is over three orders of magnitude higher than for MIC, both compounds can be monitored simultaneously, indicating that PTR-MS is an ideal tool for the online quantification of various substances present at widespread concentrations.

right
Chloroacetone is a toxic substance which was commonly used as an eye irritant in the past. In the presented measurement the headspace of pure choroacetone was injected into a polyvinyl fluoride (Tedlar®) bag filled with nitrogen. We used a Tedlar bag since these sampling bags are widely used in analytical sciences. It can be seen that although the background signal (originating from the bag) at the nominal mass of chloroacetone is rather high, the PTR-TOF 8000 instrument used for this study is still able to identify the chloroacetone (m/z 93.010). Furthermore, due to the high mass resolution we could identify the background contamination peak at 95.049 m/z as protonated phenol. Although the concentration of phenol is nearly as high as for the chloroacetone isotope and the mass difference is only 0.04 amu, both compounds can be monitored (and quantified) simultaneously. With a QMS based PTR-MS instrument the identification could be performed via the characteristic isotopic ratio for chlorine containing compounds (which is the case for many TICs).

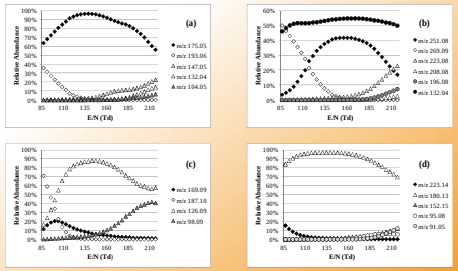
Results



bottom
Isocyanate product ion branching ratios (%) as a function of reduced electric field (E/N; this value can be changed by varying the voltage applied to the PTR drift tube and has a major influence on molecular fragmentation and detection efficiency) for

a) toluene diisocyanate (TDI)
b) methylene diphenyl diisocyanate (MDI)
c) hexamethylene diisocyanate (HDI)
d) isophorone diisocyanate (IPDI)

◊ - black represent $[M.H]^+$ and white represent $[M+H_2O]H^+$ for all four measured isocyanates.



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