

Proton-Transfer-Reaction Mass Spectrometry: Increased Selectivity in Explosives and Designer Drugs Detection

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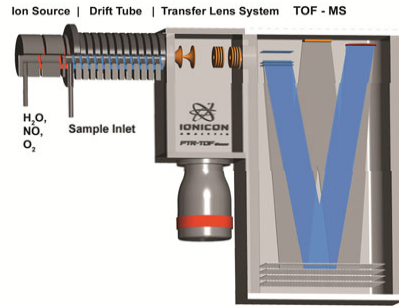
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Abstract

A relatively new area of application for **Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)** is in the field of **safety and security**, i.e. the detection of **chemical warfare agents, toxic industrial compounds, explosives, illicit and prescribed drugs**. The main reasons for the outstanding applicability of PTR-MS in this field are **high sensitivity** (down to the ppqv level) and **selectivity**, simple sample handling (no preparation necessary) and **short response time** (down to 100 ms). Details about the performance data of the latest PTR-MS instrument generation are provided here. Furthermore we present details on recent studies that introduce a **new dimension of selectivity to threat agent detection with PTR-MS**, namely bias dependence in the detection sensitivity on the reduced electric field strength E/N. Following on from our explosive research programme, we present E/N studies on **novel designer drugs**. This current work emphasizes the use of **PTR-MS as a broad-based and highly selective analytical technology for the detection of a large range of threat agents [1-5]**.



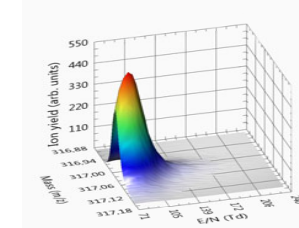
PTR-TOF 8000

Experimental Setup

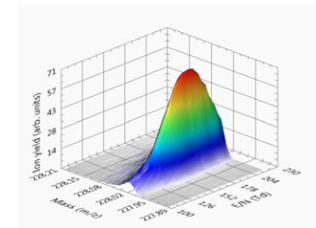
A typical PTR-TOFMS instrument consists of an ion source, where water vapor is converted into H_3O^+ in a hollow cathode discharge and an adjacent drift tube, where the actual **proton transfer** to the trace gas compounds takes place. The protonated product ions are finally analyzed and detected in a **TOF mass spectrometer**. We consecutively **improved and optimized all of these parts**, which in sum contributes to an increase in instrumental performance of over one order of magnitude (compared to the first generation of PTR-TOFMS instruments in 2009) without any decrease in mass resolution.

On the left the schematic for a **high mass-resolution** ($m/\Delta m$ up to 8000) "PTR-TOF 8000" is displayed.

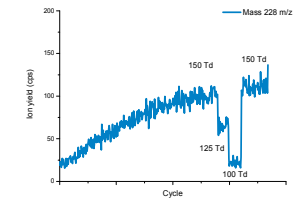
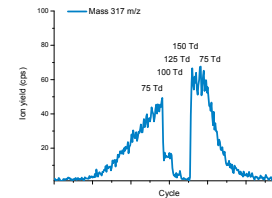
Below a picture of a **test body for the explosives measurements** is shown. These test bodies consist of aluminum foam containing a defined amount (< 1 mg) of the respective explosive and are used for **training sniffer dogs**.



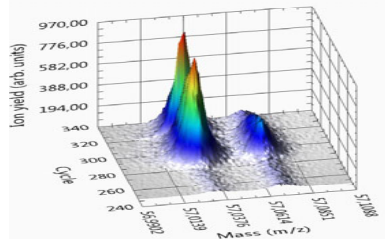
PETN



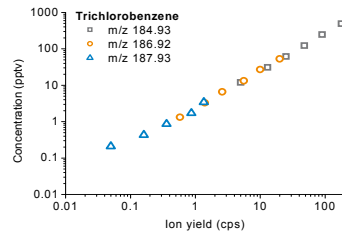
TNT



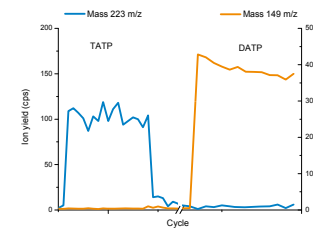
Performance Data



Measurement data obtained from a sample containing methylketene and butene to illustrate the importance of **high resolution for isobaric separation**.



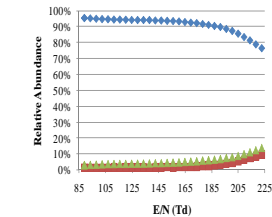
Results of the **LoD** determination utilizing a gas standard. The LoDs were calculated using the common 3σ (standard derivation) method: limit of detection is about **200 ppqv**.



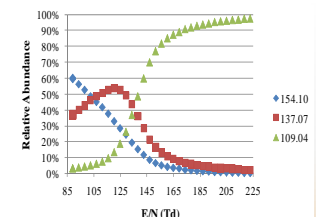
Left Investigation of two test bodies containing **TATP and DATP**, respectively. Due to the high vapor pressure of the two explosives, the **instrumental response is nearly instantaneous**.

Increased Selectivity

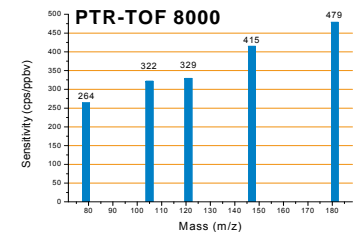
Above, E/N analyses of two test bodies containing **PETN and TNT**, respectively, are presented. The two explosives show completely opposite E/N behavior; i.e. the **E/N ratio** can be utilized as an additional criterion (besides the exact mass) for **substance identification**. Most (**designer drugs**) (examples given in the two diagrams below: the cocaine analog **dimethocaine** and the amphetamine derivative **4-fluoroamphetamine**) also possess **characteristic E/N dependent branching ratios**.



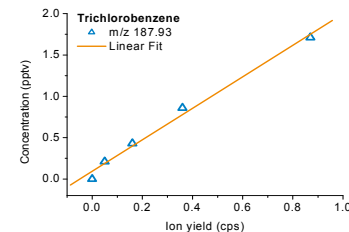
Dimethocaine



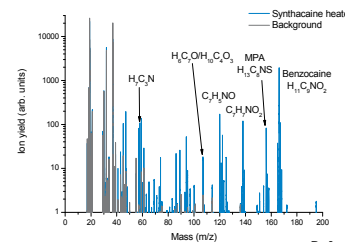
4-FA



Results of the **sensitivity** determination utilizing a gas standard. Values are stated in cps/ppbv; maximum sensitivity is about **500 cps/ppbv**.

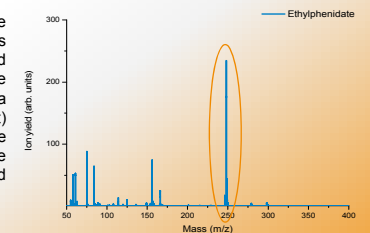


Linear visualization of the area around and below 1 pptv in order to prove linearity of the instrumental response even in the **ppqv region**.



Novel Designer Drugs

Two very **recent designer drugs** (**synthacaine**, which should imitate the effects of cocaine and is sold without any information about its composition and **ethylphenidate**, which is an analogue to the controlled methylphenidate (aka Ritalin)) were legally bought from vendors in the internet. In contrast to ethylphenidate (right), which shows a **surprisingly high purity** of the active ingredient, synthacaine (left) turns out being a **mixture of various chemicals**, with methiopropamine (MPA; structural analog of methamphetamine) being the main active ingredient and benzocaine (local anesthetic) presumably being added for the cocaine-like feeling of numbness in the nose after snorting.



References

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