

## PTR+SRI-MS

### SWITCHABLE REAGENT IONS

IONICON was first to successfully commercialize the PTR-MS technology and since 1998 IONICON is the world's leading PTR-MS manufacturer.

PTR-MS allows for real-time, online determination of absolute concentrations of volatile (organic) compounds (VOCs) in air with high sensitivity (into the low ppt range) and a fast response time (in the 40-100 ms time regime).

We developed a PTR-MS instrument using a modified ion source and drift tube design, which allows for the easy and fast switching between  $H_3O^+$ ,  $NO^+$  and  $O_2^+$  ions produced in high purity and in large quantities in this source.

This instrument is capable of measuring VOCs with all three ions at ultra low concentrations (with detection limits approaching the ppqv regime). Therefore this instrument combines the advantages of the PTR-MS technology (the superior sensitivity) with those of SIFT-MS (detection of VOCs with PAs smaller than that of the hydronium ion and the capability to distinguish between isomeric compounds)

## Increased number of measurable substances

Proton transfer reactions from  $H_3O^+$  are generally limited by the proton affinity of the molecule of interest. With the newly introduced PTR+SRI-MS it is now possible to analyze substances that could not be ionized with PTR-MS using exclusively hydronium as reagent ions.

Here one can see the advantage of utilizing  $O_2^+$  as primary ions for just two examples:

**Ethylene**, is the most produced organic compound in the world. It is used not only for the manufacturing of various "plastic products", but also in food industry (fruit ripening), as a welding gas, as an anesthetic agent, etc.

**Acetylene** is also an important component of everyday life as it is commonly used in industry as a chemical building block.

Both molecules possess a lower proton affinity than  $H_3O^+$  and can therefore not be ionized via proton transfer. However, as the ionization energies of both substances lie well below the ionization energy of  $O_2^+$ , charge transfer ionization will occur with these reagent ions.

This means that the amount of substances that can be analyzed with IONICON's instruments is now seriously increased without losing the outstanding sensitivity for which we are famous since many years.

## ppqv detection limit

With our hollow cathode ion source we are able to generate outstandingly intense beams of reagent ions at very high purity levels:

$H_3O^+$	▶	$40 \times 10^6$ cps
$NO^+$	▶	$60 \times 10^6$ cps
$O_2^+$	▶	$50 \times 10^6$ cps

These extremely high reagent ion count rates finally lead to a detection limit in the ppqv region.

We just recently carried out a series of measurements where we carefully determined the detection limit and the sensitivity of an IONICON High-Sensitivity PTR-MS instrument.

Fig.1 shows the results from measurements utilizing  $H_3O^+$  reagent ions whereas the data plotted in Fig.2 was obtained from reactions with  $NO^+$  reagent ions.

As this work has just been submitted in great detail to IJMS (Jordan et al. 2009), here we just want to point out the two main outcomes, namely

## Sensitivity: nearly 1000 cps/ppbv Detection limit: $10^2$ ppqv regime

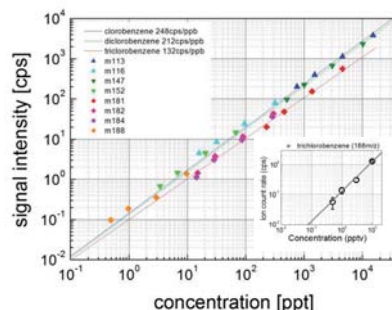


Fig.1 Correlation plot (measured ion count rates versus absolute concentration) for chlorobenzene and trichlorobenzene for  $H_3O^+$  reagent ions measured with an integration times between 7 and 180 s. The small diagram shows the trichlorobenzene data close to the detection threshold after subtraction of background signal.

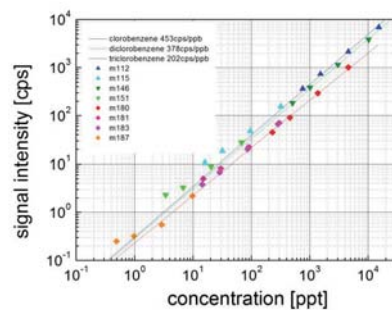


Fig.2 Correlation plot (measured ion count rates versus absolute concentration) for chlorobenzene and trichlorobenzene for  $NO^+$  reagent ions measured with an integration times between 7 and 180 s.

## Separation and identification of isomers

The analysis of isomeric aldehydes and ketones with common PTR-MS is a quite delicate task as these compounds yield, by definition, on the same nominal masses. With the novel PTR+SRI-MS this problem can be solved in a very sophisticated way utilizing  $NO^+$  as reagent ions.

Fig.3 shows a comparison of mass spectra obtained from 8 aldehydes using  $H_3O^+$ ,  $NO^+$  and  $O_2^+$ . It can be easily seen that  $NO^+$  leads to the simplest spectrum mainly giving dehydrogenated cations (M-H) $^+$ .  $O_2^+$  on the other hand reacts via exothermic charge transfer resulting in strong fragmentation, whereas proton transfer from  $H_3O^+$  produces mostly protonated parent molecules (MH) $^+$ .

The situation now gets very interesting if we compare the  $NO^+$  results with those obtained from studies on ketones. In Fig.4 we see that  $NO^+$  reacts with ketones mainly via the formation of M. $NO^+$  and simply M $^+$  (ratio depending strongly on the collision energy, i.e. the E/N ratio).

These observations lead to the conclusion, that with PTR+SRI-MS it is possible to separate and analyze isomeric compounds (acetone/propanal and butanone/butanal in the example).

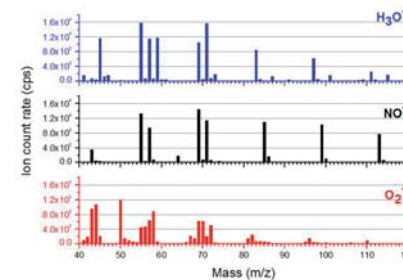


Fig.3 Mass spectra from reaction with 8 aldehydes for  $H_3O^+$ ,  $NO^+$  and  $O_2^+$  reagent ions.

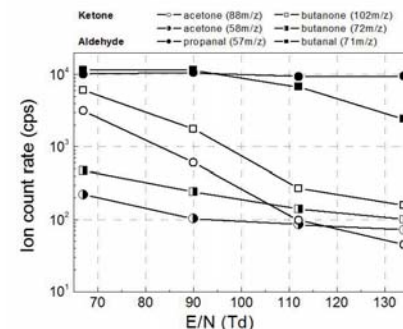


Fig.4 Ion count rates versus the reduced field strength E/N. The ketones are measured at the association complex mass 88 for acetone and 102 for butanone and at the parent masses. In contrast, the respective isomeric aldehydes propanal and butanal react with  $NO^+$  exclusively to dehydrogenated product ions at masses 57 and 71.



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