

# High Purity $\text{H}_3\text{O}^+$ Reactant Ions Enable Simple Interpretation of Vocus PTR-TOF Data

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## Online CI-MS Analysis of Air Demands Well Understood Ion Chemistry

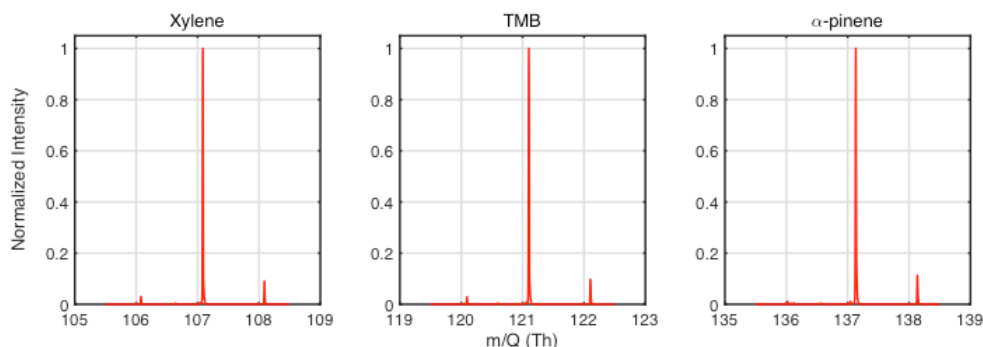
Air samples that contain volatile organic compounds (VOCs) are often complex mixtures of tens or hundreds of different trace compounds. Traditional techniques for analysis of such samples require labor-intensive sample preparation and chromatographic separation, thus limiting measurement throughput and/or the time resolution of the VOC measurements. In contrast, chemical ionization mass spectrometry (CI-MS) can quantitatively measure VOCs in real-time with sub-second time resolution. These fast, online capabilities stem from easy-to-understand ion chemistry that allows ionization and mass spectral detection of VOCs without the need for sample preparation or chromatographic separation.

In CI-MS, air that contains neutral, gas-phase analyte molecules is directly sampled into the mass spectrometer. Analyte

molecules are ionized by way of chemical reactions with high-concentration reactant ions (aka primary ions or reagent ions) under controlled conditions. The analyte ions produced in these reactions are subsequently measured by a mass analyzer, which determines the ions' mass/charge values and abundances. The level of difficulty of interpreting the mass spectrum depends on the complexity of the ion chemistry - which is largely determined by the reagent ion of choice - and the purity of the ion source. For a given ion chemistry, the purer the source of reactant ions, the easier the spectrum is to interpret.

## High Purity Reactant Ions Make Vocus Data Readily Interpretable

Proton transfer reaction mass spectrometry (PTR-MS) is a type of CI-MS that is widely used for online detection of VOCs. The Vocus PTR-TOF is an ultra-sensitive PTR-MS that combines TOFWERK's proprietary Vocus reactor technology and a



**Figure 1 Comparing protonated and non-protonated mass spectral signals for various VOCs to measure Vocus PTR-TOF ion source purity.** Data for the three VOCs show the major protonated peak ( $MH^+$ ), the minor charge transfer peak ( $M^+$ ), and isotope peaks consistent with molecular composition. Based on the ratios of the displayed protonated to non-protonated peaks, the ion source purity when operated at maximum sensitivity is >98%, enabling simple interpretation of Vocus PTR-TOF data.

time-of-flight mass analyzer. High abundance  $H_3O^+$  reactant ions are produced with water vapor in a low-pressure plasma in a dedicated ion source region. The generated reactant ions transferred into a recombination region before entering the ion-molecule reaction region where  $H_3O^+$  ions transfer protons to neutral VOC analyte molecules, creating VOC analyte ions that can be measured by the mass analyzer.

In practice, PTR mass spectra can be corrupted by spectral peaks originating from parasitic reactant ions (e.g.,  $NO^+$ ,  $O_2^+$ ), generated from either back-diffusion of air into the primary plasma region or the reaction of excited radicals exiting the ion source and meeting the sample flow. The presence of spurious  $O_2^+$  and  $NO^+$  ions complicate the spectrum because both are capable of ionizing common VOCs via charge transfer pathways to yield different (non-protonated) product ions or driving fragmentation reactions.

The purity of the reagent ion source used for PTR-MS can be

determined by either a) direct comparison of  $O_2^+$  and  $NO^+$  signal to that of  $H_3O^+$  or b) the ratio of the protonated and non-protonated signals of targeted compounds. The latter approach better reflects the reaction conditions in the IMR as additional quenching time during transit through the reactor can distort the actual reactor conditions and the observed relative abundances of  $H_3O^+$ ,  $O_2^+$ , and  $NO^+$ .

Figure 1 compares protonated to non-protonated peaks in Vocus PTR-TOF data for a series of VOCs of varied mass/charge and having different functional groups. In all cases, the VOCs are charged predominantly by protonation, with only minor contributions (~1-3%) from spurious charge transfer reactions, demonstrating the high purity of the Vocus ion source. At this high purity, Vocus mass spectra are dominated by protonated peaks and free of significant contributions from non-PTR reaction and therefore easily interpreted and quantified.

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