

Ultra-Fast Time Response with the Vocus PTR-TOF

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Chemical ionization mass spectrometry (CI-MS) is a real-time trace gas analysis method that is well suited for applications that characterize fast-changing signals, such as process line monitoring, measurements from aircraft or mobile labs, breath analysis, and eddy covariance flux measurements. The Vocus proton transfer reaction time-of-flight mass spectrometer (PTR-TOF) is a CI-MS that can measure molecules with a wide range of volatilities, starting with the most volatile organic compounds (VOCs) and extending to intermediate- (IVOC), semi- (SVOC), and low-volatility organic compounds (LVOC).

In order to accurately record fast changes in the concentrations of VOCs of interest, the time response of a CI-MS must be faster than the transient event being observed. As the volatility (or vapor pressure) of molecules decreases, their 'stickiness' increases. Interactions between semi- and low-volatility compounds and the walls of the ion molecule reactor can lead to "smearing" of their recorded temporal profiles. This effect generally depends on a molecule's saturation vapor concentration

and/or the presence of chemical functionalities that interact with materials used in the ion molecule reactor. As the volatility of sampled molecules decreases the potential for significant smearing of the temporal profile increases.

Among PTR mass spectrometers, the Vocus PTR-TOF offers notably fast time response. Traditional drift tube-based PTR-MS often use a long, low-pressure inlet line that leads to unwanted wall interactions and - consequently - slow time response due to the limited flow rate into the reaction cell (10 - 30 sccm). In contrast, the Vocus PTR-TOF utilizes a high sample flow from an axial sample introduction system, of which 100 sccm is directly sampled into the ion molecule reactor. Additionally, the Vocus reaction cell is heated to promote the rapid repartitioning of condensed or adsorbed material off the reactor surfaces, further ensuring excellent time response for lower volatility compounds.

Figure 1 shows observed time response behavior for 3 IVOCs measured at two different reactor body temperatures. Time responses were measured by sampling a bag

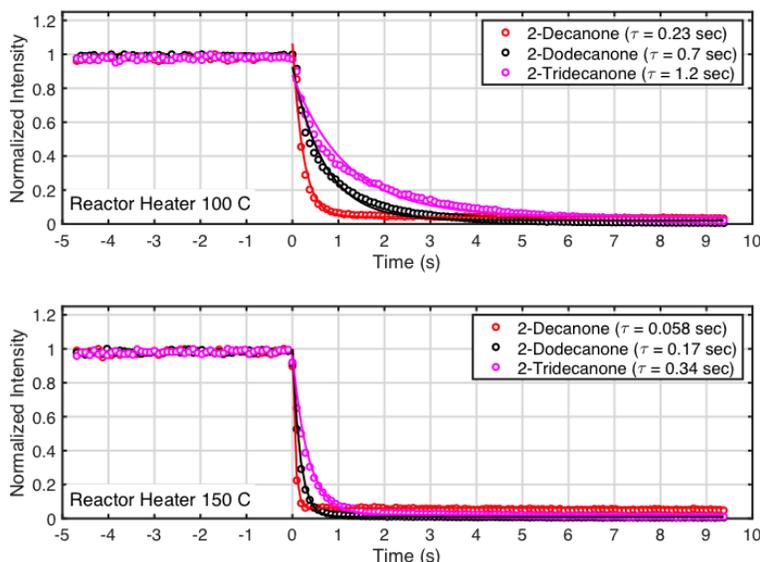


Figure 1 Time response of the Vocus PTR-TOF for low volatility compounds measured at two different reactor temperatures. Open circles show 100 ms data points normalized to their starting values. Solid lines are the exponential fits used to calculate the time constants τ shown in the legend. Note that the reactor body temperature is an upper limit to the reaction cell gas temperature due to finite heat transfer across the walls of the glass tube and transfer to the sample gas.

containing 2-decanone, 2-dodecanone and 2-tridecanone at concentrations of approximately 40 ppbv. After all signals had equilibrated, sampling was rapidly changed from the bag to clean air generated by the inbuilt zero air system ($t = 0$ s). Mass spectral data were continuously acquired at 10 Hz to observe the time required for the signals to transition from the equilibrium value to zero. The observed decay in the recorded signal of each compound is shown with open circles. The instrument-only time constants, τ , determined from the exponential fits (solid lines) are displayed in the legend.

At a reactor body temperature of 100 C, time constants for all three IVOCs are on the order of 1 second or better. Increasing the temperature of the reactor to 150 C

leads to clear improvement for all three compounds. The time constant of the most volatile compound, 2-decanone, approaches the flushing time of the reaction cell, which is approximately 50 ms.

The response time for semi-volatile compounds can also depend on functional groups of the molecule. Some functional groups, for example acids, interact more strongly with surfaces resulting in a slower response time than saturation vapor concentrations alone would suggest. Figure 2 shows the time response of the Vocus PTR-TOF for compounds containing different functionalities, including siloxanes and acids. Even for pinonic acid, an oxidation product derived from monoterpenes, the Vocus has a time response of less than 2 seconds.

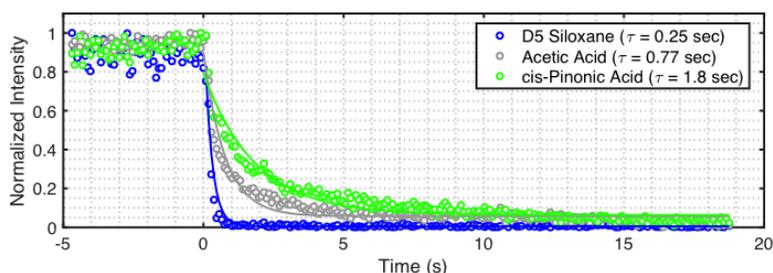


Figure 2 Time response of a Vocus PTR-TOF for VOCs having different functional groups. (Blue) D5 Siloxane ($C_{10}H_{30}O_5Si_5$) found in many consumer products; (Grey) Acetic acid ($C_2H_4O_2$), a ubiquitous organic acid found in the atmosphere; (Green) Pinonic acid ($C_{10}H_{16}O_3$), a semi-volatile oxidation product derived from the oxidation of monoterpenes. Data were recorded at a reactor heater body temperature of 150 C.

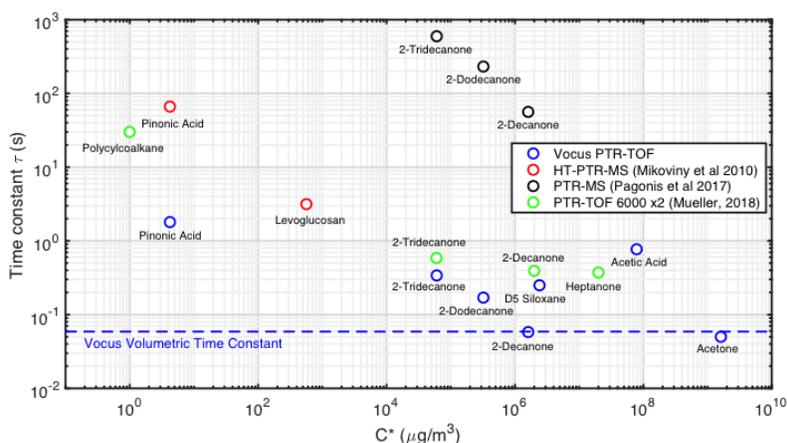


Figure 3 VOC time constants for different generations and types of PTR mass spectrometers. Blue points were measured on a Vocus PTR-TOF. The blue dashed line shows the theoretical decay constant based on the reaction cell volume and the volumetric flow rate of the Vocus reactor. For many VOCs the response time of Vocus is determined by the flush out time of the reactor. For compounds with lower volatility or functionalities which interact more strongly with surfaces, the time constant is slightly longer. Reported values for different PTR mass spectrometers are also plotted. At high C^* ($>10^8 \mu\text{g}/\text{m}^3$), which correspond to 'non-sticky' VOCs, PTR-MS generally have time constants which approach the volumetric flushing rate of the reaction cell ($\tau < 1 \text{ s}$). As the saturation vapor concentration decreases the different instruments' responses diverge from the Vocus, which responds at least an order of magnitude faster at $C^* \approx 1 \mu\text{g}/\text{m}^3$.

Figure 3 compares measured Vocus PTR-TOF time constants for VOCs with a range of saturation vapor concentrations, C^* , to values reported with different PTR mass spectrometers. For non-sticky VOCs, $C^* > 10^8 \mu\text{g}/\text{m}^3$, PTR-MS generally have time constants which approach the volumetric flushing rate of the instrument's reaction cell ($\tau < 1 \text{ s}$). As volatility decreases the reported response times of the other PTR-MS become longer than those of the

Vocus PTR-TOF. In the range near $C^* \approx 1 \mu\text{g}/\text{m}^3$, the Vocus is shown to be approximately an order of magnitude faster.

The combination of its efficient inlet system, heated reaction cell, and high sensitivity makes the Vocus PTR-TOF the optimum detector for high throughput or highly time resolved measurements of low volatility organic compounds.

References

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