

Supplement of

**Product Ion Distributions using H_3O^+ PTR-ToF-MS:
Mechanisms, Transmission Effects, and Instrument-to-
Instrument Variability**

Michael F. Link, et al.

Correspondence to: Michael F. Link (michael.f.link@nist.gov)

Step-by-step guide detailing how to measure and quantify PIDs.

Below is a step-by-step guide on how to measure and quantify PIDs from VOC calibration sources based on the method described in the main text. Where a gas chromatograph (GC) is used, the guide assumes the user knows how to interface the GC to the mass spectrometer. The guide also assumes that the user can configure the sample collection timing for the mass spectrometer.

Step 1: Measure VOC Sample

The purpose of this step is to measure a VOC sample (the “target analyte”) for which PIDs are to be quantified from. This measurement is performed with the mass spectrometer. If the user has a GC, multi-component gas standard mixtures can be used as the VOC sample. If the user does not have a GC, single-component gas mixtures or mixtures of no more than two analytes that do not share any product ions (as reported in literature or from mechanistic reasoning) should be used.

Using a GC:

- (1) Set the sample acquisition time on the data acquisition software for the mass spectrometer between 2 Hz to 5 Hz. Ensure that the sample collection time exceeds the GC sample elution time.
- (2) Acquire a 1 L sample of calibration gas from a gas cylinder, evaporated liquid, or permeation device where the concentration of the target analyte is greater than 1 nmol mol⁻¹ and less than 10 nmol mol⁻¹.
 - a. Note: Multi-component gas mixtures can be used with GC separation. Analytes in multi-component mixtures with similar retention times may be difficult to quantify PIDs from even with a GC.
 - b. Note: The concentration range and sample collection volume prescribed here is for the commercial GC system used for the instruments in this study. The concentration ranges and collection volumes prescribed for the GC here equates to 0.05 nmol to 0.5 nmol (for 1 nmol mol⁻¹ to 10 nmol mol⁻¹ with 1 L collection) total analyte sampled by the mass spectrometer.
- (3) Separate the target analyte using a gas-chromatography method. Good separation of the target analyte from closely eluting species is important for accurate determination of PIDs. We define “good separation” where two closely eluting peaks, with a peak full-width half-maximum resolution of 2 s, are separated by a peak-to-peak distance no closer than 4 s. Determination of PIDs from peaks that have eluted closer and with poorer resolution is possible, but subtracting out the influence of the closely eluting peak from the target analyte becomes increasingly due to the increasing influence of background mass spectral interferences.

Without a GC:

Figure S1 is included as a visual aid to the instructions provided below.

- (1) Set the sample acquisition time on the data acquisition software for the mass spectrometer to a 10 s collection rate. This rate minimizes file size while allowing the user to quickly see if the VOC mixture has passivated the sampling system, but any other rate can be used.
- (2) Connect the VOC source to an 8 cm section of PFA tubing that connects to a PFA tee (see Figure S1). Connect a source of ultra-pure zero air to one side of the PFA tee. Connect this tee to another section of 13 cm PFA tube (for gas mixing) that is connected to another tee. One side of this tee serves as the exhaust and should be directed to a fume hood if possible. The other side of this tee connects to the sample inlet for the mass spectrometer.
 - a. Note: Lengths of tubing reported here are recommended. Longer lines of tubing may require longer passivation times.
- (3) Dilute the VOC gas mixture so the analyte concentration is approximately 10 nmol mol⁻¹.
- (4) Ensure that the sampling inlet is fully passivated by measuring the VOC mixture over a period of approximately 5 minutes and observing minimal change in steady-state concentration.
- (5) Collect a VOC sample to generate the “signal” mass spectrum from.

- (6) Remove the VOC mixture source (capping the VOC mixture introduction port if necessary) and overflow the the sample inlet with zero air for 5 minutes. After 5 minutes collect a sample of zero air to generate a “background” mass spectrum.

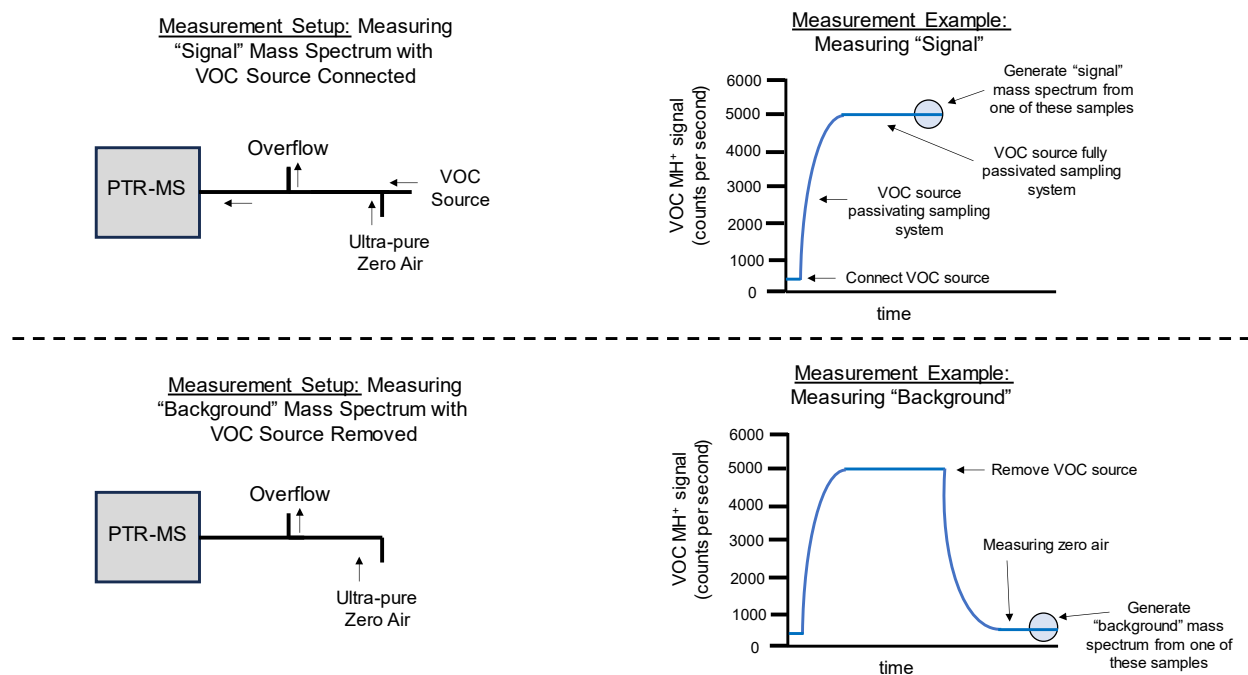


Figure S1: Conceptual diagram showing the method of measuring a VOC sample to quantify a PID without using a GC. (top panel) The measurement setup is shown for connecting both the VOC source and zero air dilution gas to the sampling inlet of the mass spectrometer (PTR-MS). Arrows indicate the direction of gas flow. The measurement example on the right shows the ion signal for the H^+ adduct of a VOC target analyte. Before the VOC source is connected a background signal can be observed for the target analyte. Once the VOC source is connected there is some sampling system passivation time before a steady-state concentration is reached. Mass spectra that are collected once steady-state has been achieved (indicated by the blue highlighted circle) are appropriate for use as the “signal” mass spectrum for the PID calculation. (bottom panel) Once the data for the “signal” mass spectrum has been collected the VOC source can be removed from the sampling line and a measurement of zero air can be acquired for determining the “background” mass spectrum in the PID calculation. Mass spectra that are collected once steady-state background signal has been achieved (indicated by the blue highlighted circle) are appropriate for use as the “background” mass spectrum for the PID calculation.

Step 2: Generate “Isolated” Mass Spectrum

This step assumes the user can generate time series of integrated peak areas for high-resolution (i.e., greater than unit mass resolution) ions identified by m/Q values with a corresponding elemental formula in the mass spectrum. High-resolution peak fitting and integration should be done with a detailed ion peak list that includes background ions, target analytes, and all potential product ions. High-resolution data is most useful for quantifying PIDs, but unit-mass resolution data can also be used.

- (1) Choose a single representative mass spectrum from when the VOC was being sampled to act as the “signal” mass spectrum and another mass spectrum from when the VOC was not being sampled to act as the “background” mass spectrum (see Figure 1a from the main text for a GC measurement or Figure S1 for a non-GC measurement).
 - a. Note: When using a GC, if another analyte elutes close (i.e., peak-to-peak distance of < 5 s) to the target VOC the representative “background” mass spectrum should be defined at the peak-to-peak valley between the target analyte and the closely eluting peak.

- (2) Subtract the ion signals in the “background” mass spectrum from the “signal” mass spectrum to obtain the “isolated” mass spectrum. (See Figure 1b in the main text).

Step 3: Calculate PID

- (1) Normalize all the ion signals in the “isolated” mass spectrum to the largest signal to obtain a normalized mass spectrum.
- (2) Account for all of the ions that make a contribution of > 0.01 to the normalized mass spectrum. We will call these ions the “likely product ions”.
- (3) Classify which of the likely product ions can be identified as one of the product ions in the “product ion identity” column in Table 1 in the main text.
 - a. Note: Fragments and “other ions” are going to be most difficult to confidently identify. It is not recommended to classify any ion as “other” unless the user consistently observes this product ion from several target analytes or sees significant changes in the abundance of the product ion from ionization of a target VOC under different conditions of E/N.
- (4) If the user is left with unclassified likely product ions, after accounting for all of the ions that can be classified via their “product ion identity”, then the user should evaluate if there is a possible mechanism for the generation of the product ion that was not considered here. However, if the user cannot determine the possible source of the product ion, then it should not be included in the PID calculation.
- (5) Once all of the product ions have been accounted for the normalized integrated peak areas for each ion should be added together to form the total product ion signal. The normalized integrated peak area of each product ion divided by the total product ion signal will then generate the product ion distribution.
- (6) Following the formatting of the H_3O^+ PID Library, the PID for the VOC can be recorded with m/Q and elemental formula corresponding to the product ions (columns F through Q) and the associated product ion contribution (columns R through AC).

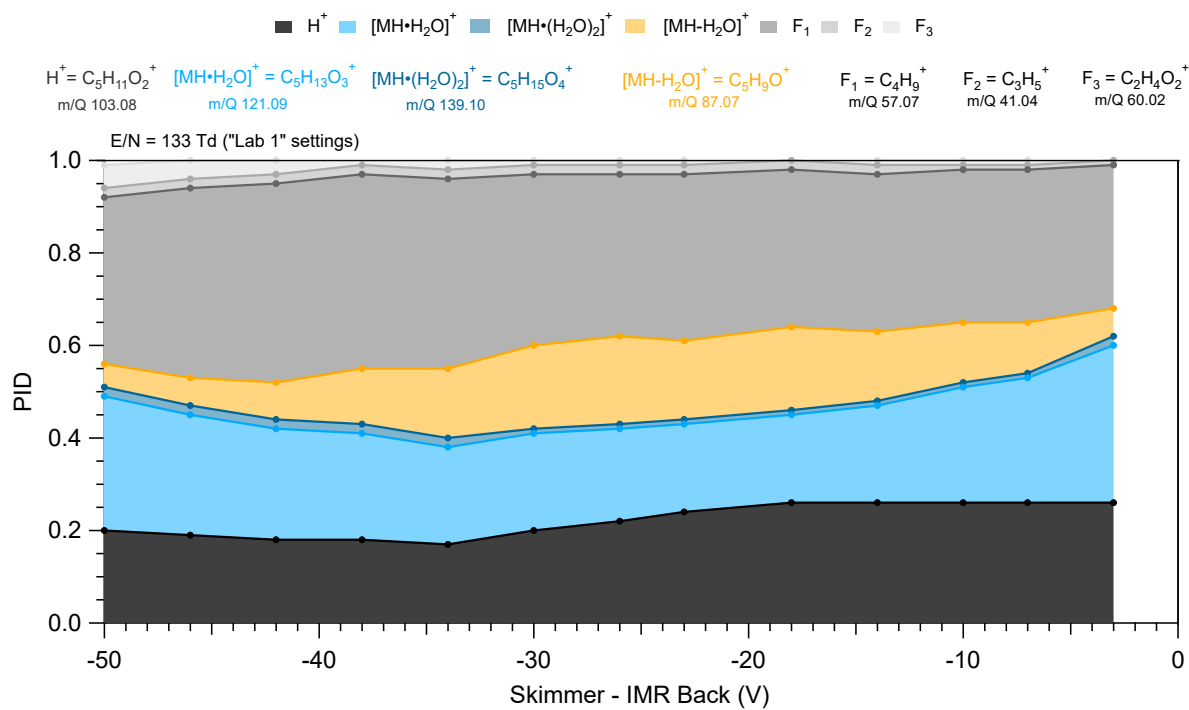


Figure S1: Pentanoic acid PID as a function of the voltage difference between the Skimmer and IMR Back components (i.e., ΔV_1 from Fig. 2 in the main text).

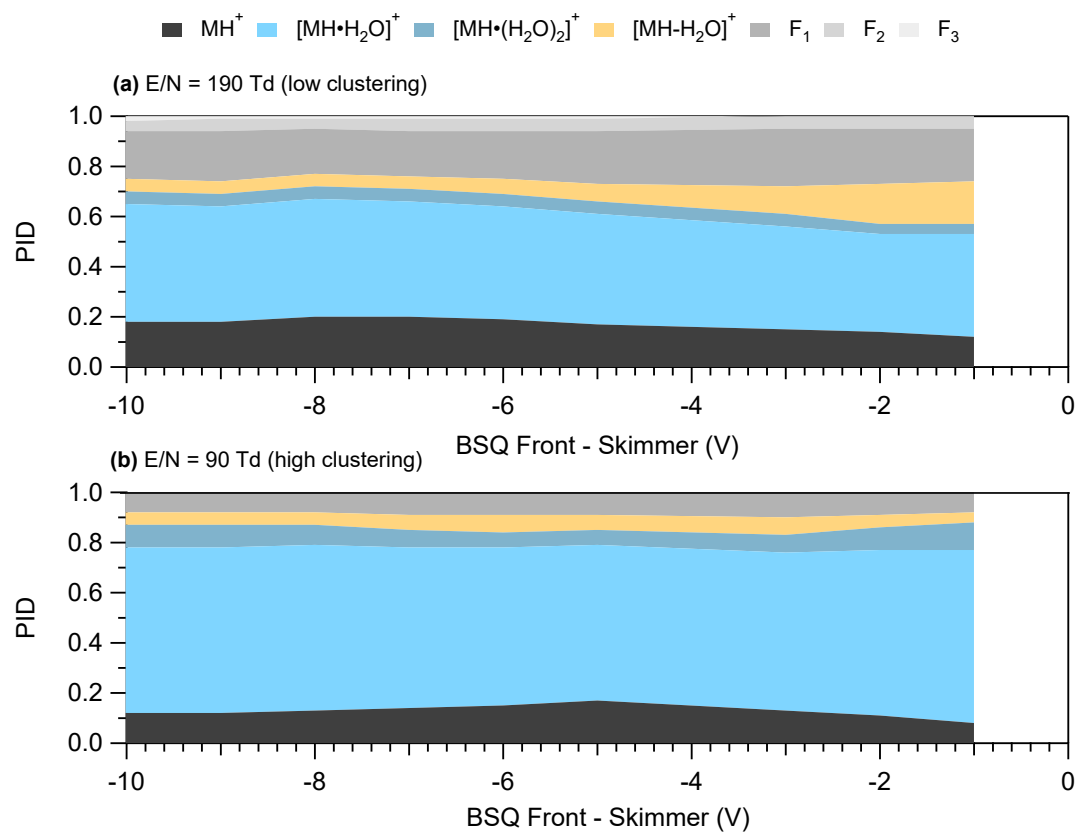


Figure S2: Pentanoic acid PID as a function of the voltage difference between the BSQ Front and Skimmer components (i.e., ΔV_2 from Fig. 2 in the main text).

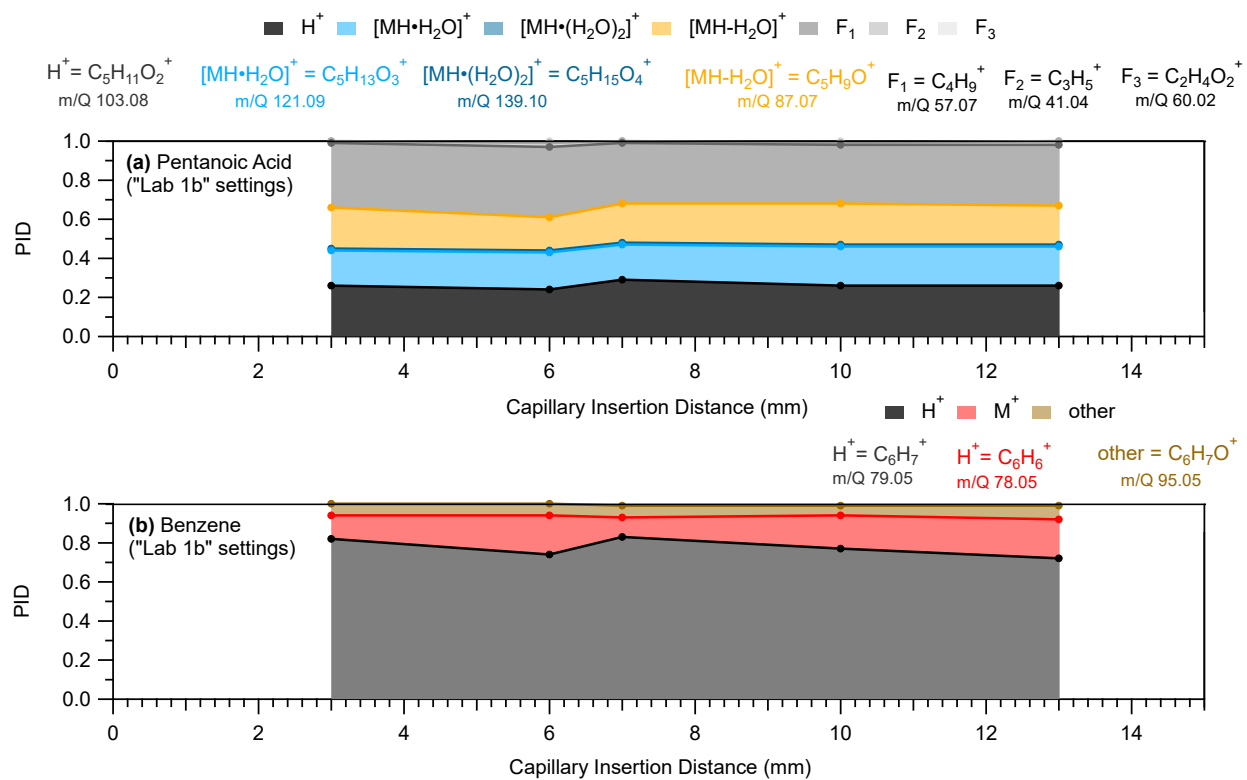


Figure S3: PIDs for (a) pentanoic acid and (b) benzene as a function of capillary insertion distance.

Table S1: Average and standard deviations (1 σ) of PIDs for select VOCs in main text Figure 8.

VOC (molecular formula)	Product Ions			
	MH ⁺	Water Clusters	Charge and Hydride Transfer	Fragments and Other
Acetaldehyde (C ₂ H ₄ O)	C ₂ H ₃ O ⁺ = 0.85 ± 0.10 (N = 5)	C ₂ H ₇ O ₂ ⁺ = 0.15 ± 0.10 (N = 5)		
Acetone (C ₃ H ₆ O)	C ₃ H ₇ O ⁺ = 0.94 ± 0.04 (N = 11)	C ₃ H ₉ O ₂ ⁺ = 0.04 ± 0.03 (N = 9)	C ₂ H ₃ O ⁺ = 0.05 ± 0.04 (N = 5)	
Isoprene (C ₅ H ₈)	C ₅ H ₉ ⁺ = 0.75 ± 0.21 (N = 10)		C ₅ H ₈ ⁺ = 0.04 ± 0.04 (N = 7) C ₅ H ₇ ⁺ = 0.10 ± 0.10 (N = 9)	C ₃ H ₅ ⁺ = 0.11 ± 0.09 (N = 7) C ₃ H ₃ ⁺ = 0.09 ± 0.09 (N = 6)
Toluene (C ₇ H ₈)	C ₇ H ₉ ⁺ = 0.69 ± 0.10 (N = 9)		C ₇ H ₈ ⁺ = 0.12 ± 0.11 (N = 7) C ₇ H ₇ ⁺ = 0.14 ± 0.05 (N = 9)	C ₆ H ₇ O ⁺ = 0.10 ± 0.03 (N = 7)
Ethanol (C ₂ H ₆ O)	C ₂ H ₇ O ⁺ = 0.50 ± 0.12 (N = 7)	C ₂ H ₉ O ₂ ⁺ = 0.33 ± 0.18 (N = 6) C ₂ H ₁₁ O ₃ ⁺ = 0.03 ± 0.01 (N = 2)	C ₂ H ₅ O ⁺ = 0.38 ± 0.26 (N = 4)	
Acetonitrile (C ₂ H ₃ N)	C ₂ H ₄ N ⁺ = 0.82 ± 0.20 (N = 10)	C ₂ H ₆ NO ⁺ = 0.2 ± 0.2 (N = 9)		
α -pinene (C ₁₀ H ₁₆)	C ₁₀ H ₁₇ ⁺ = 0.42 ± 0.07 (N = 9)			C ₆ H ₉ ⁺ = 0.46 ± 0.07 (N = 9) C ₇ H ₉ ⁺ = 0.08 ± 0.09 (N = 7) C ₆ H ₇ ⁺ = 0.03 ± 0.02 (N = 8) C ₇ H ₁₁ ⁺ = 0.04 ± 0.02 (N = 7)
m-xylene (C ₈ H ₁₀)	C ₈ H ₁₁ ⁺ = 0.81 ± 0.16 (N = 6)		C ₈ H ₁₀ ⁺ = 0.10 ± 0.11 (N = 6)	C ₇ H ₇ ⁺ = 0.10 ± 0.04 (N = 4)

			$C_8H_9^+ = 0.02 \pm 0.01$ (N = 5)	
Methyl ethyl ketone (C ₄ H ₈ O)	$C_4H_9O^+ = 0.90 \pm 0.06$ (N = 8)	$C_4H_{11}O_2^+ = 0.08 \pm 0.06$ (N = 6)		$C_4H_7^+ = 0.08 \pm 0.03$ (N = 3) $C_2H_3O^+ = 0.05 \pm 0.01$ (N = 2)
Acrylonitrile (C ₃ H ₃ N)	$C_3H_4N^+ = 0.94 \pm 0.04$ (N = 7)	$C_3H_6NO^+ = 0.06 \pm 0.04$ (N = 7)		
Limonene (C ₁₀ H ₁₆)	$C_{10}H_{17}^+ = 0.40 \pm 0.08$ (N = 6)			$C_6H_9^+ = 0.50 \pm 0.06$ (N = 6) $C_6H_7^+ = 0.03 \pm 0.02$ (N = 6) $C_7H_{11}^+ = 0.07 \pm 0.03$ (N = 5)
1,2,4- trimethylbenzene (C ₉ H ₁₂)	$C_9H_{13}^+ = 0.80 \pm 0.16$ (N = 5)		$C_9H_{12}^+ = 0.16 \pm 0.12$ (N = 4) $C_9H_{11}^+ = 0.01 \pm 0.01$ (N = 5)	$C_8H_9^+ = 0.06 \pm 0.03$ (N = 5)