Designation: D8460 – 22

Standard Test Method for
Quantification of Volatile Organic Compounds Using Proton Transfer Reaction Mass Spectrometry[1]

1. Scope

1.1 This test method describes a technique of quantifying the results from measuring various volatile organic compound contents using a chemical ionization mass spectrometer resulting in the production of positively charged target compound ions. Depending on the nature of production of so-called primary ions, the associated instruments having the capability to perform such analyses are either named Proton Transfer Reaction Mass Spectrometers (PTR-MS), Selected Ion Flow Tube Mass Spectrometers (SIFT-MS) or, in the most generic term, Mid-pressure chemical ionization mass spectrometers (MPCI-MS). Within this standard, the term PTR-MS is used to represent any of these instrumentations.

1.2 Either of the instrument types can be used with the two main mass analyzers on the market, that is, with either quadrupole (QMS) or time-of-flight (TOFMS) mass analyzer. This method relates only to the quantification portion of the analysis. Due to large differences in user interfaces and operating procedures for the instruments of the main instrument providers, the specifics on instrument operation are not described in this method.

1.3 Details on the theoretical aspects concerning ion production and chemical reactions are included in this standard as far as required to understand the quantification aspects and practical operation of the instrument in the field of vapor intrusion analyses. Specifics on the operation and/or calibration of the instrument need to be identified by using the user's manual of the individual instrument vendor. A comprehensive discussion on the technique including individual mass-line interferences and in-depth comparison with alternate methods are given in multiple publications, such as Yuan et al. (2017) (**1**) and Dunne et al. (2018) (**2**)[2].

1.4 *Units*—Values stated in SI units are to be regarded as standard. No other units of measurement are included in this

standard. Reporting of test results in units other than SI shall not be regarded as nonconformance with this standard.

1.5 All observed and calculated values shall conform to the guidelines for significant digits and rounding established in Practice D6026.

1.5.1 The procedures used to specify how data are collected/recorded or calculated in the standard are regarded as the industry standard. In addition, they are representative of the significant digits that generally should be retained. The procedures used do not consider material variation, purpose for obtaining the data, special purpose studies, or any considerations for the user's objectives; and it is common practice to increase or reduce significant digits of reported data to be commensurate with these considerations. It is beyond the scope of this standard to consider significant digits used in analysis methods for engineering data.

1.6 This standard may involve hazardous materials, operations, and equipment. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D3740 Practice for Minimum Requirements for Agencies

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

3. Terminology

3.1 *Definitions:*

3.1.1 For ease of reading, the term PTR-MS is used to reflect any variations of instrumentation as described in 1.1 and 1.2.

3.1.2 For definitions of common technical terms used in this standard, refer to the guidelines in Practice D1357 and Terminology D653.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *gas analysis, n*—involves multiple gas measurements including calibration and zero gas background subtraction, therefore involves multiple gas measurements.

3.2.2 *gas measurement, n*—an analysis performed with a PTR-MS without calibration nor zero gas background subtraction.[5]

3.2.3 *ion molecule reactor, n*—the instrument part within the PTR-MS where ionization reactions of the target molecules using primary ions happen

3.2.4 *ZeroAir, n*—a gas determined to be free of any interfering substances at the reporting limit of the project.

3.2.4.1 *Discussion*—For example, the PTR-MS can be used to perform the analysis or an equivalent methodology or the certificate can be used in case of a certified cylinder.[6]

3.3 *Abbreviations:*

3.3.1 *CI-MS*—chemical ionization - mass spectrometer or spectrometry

3.3.2 *DOD*—United States Department of Defense

3.3.3 *DOE*—United States Department of Energy

3.3.4 *EPA*—United States Environmental Protection Agency

3.3.5 *FEP*—fluorinated ethylene propylene

3.3.6 *GC*—gas chromatography

3.3.7 *ICAL*—initial multipoint calibration

3.3.8 *IMR*—ion molecule reactor

3.3.9 *LCS*—laboratory control sample

3.3.10 *MDL*—method detection limit

3.3.11 *MS*—mass spectrometer

3.3.12 *NIST*—National Institutes of Standards and Technology

3.3.13 *PEEK*—polyetheretherketone

3.3.14 *PFA*—polyfluoroalkoxy alkane

3.3.15 *PTFE*—polytetrafluoroethylene

3.3.16 *PTR-MS*—proton transfer reaction - mass spectrometer or spectrometry

3.3.17 *QMS*—quadrupole mass spectrometer

3.3.18 *SDS*—safety data sheet

3.3.19 *SIFT-MS*—selected ion flow tube - mass spectrometer or spectrometry

3.3.20 *TOFMS*—time-of-flight mass spectrometer

3.3.21 *VI*—vapor intrusion

3.3.22 *VOC*—volatile organic compound

3.4 *Symbols Used in Equations:*

3.4.1 A—a target compound (analyte)

3.4.2 AH^+—a protonated target compound

3.4.3 R—reagent ion (primarily hydronium)

3.4.4 $C_V^N(A)$= [A]—number concentration (molecules/mL) of a neutral A in the ion molecule reactor

3.4.5 $C_V^V(A)$—mixing ratio or concentration of a constituent ion sample air (mL/L)

3.4.6 $I(AH^+)$—signal intensity, that is, ion count rates (ions/s)

3.4.7 $E(AH+)$—ion transmission efficiencies through the mass spectrometer

3.4.8 k—ion–molecule reaction rate constant (molecules mL^{-1} s^{-1})

3.4.9 t—reaction time (s)

3.4.10 τ—dwell time (s)

3.4.11 $[air]_R$—C_V^N (air) number concentration of air in the ion molecule reactor (molecules/mL)

3.4.12 C_{cal}—calibration concentration (nL/L)

3.4.13 p_R—pressure of the ion molecule reactor (mbar)

3.4.14 T_R—temperature of the ion molecule reactor (K)

3.4.15 U_R—voltage of the ion molecule reactor (V)

3.4.16 μ—ion mobility (m^2 V^{-1} s^{-1})

3.4.17 μ_0—reduced ion mobility (cm^2 V^{-1} s^{-1}) at standard conditions of p_0 and T_0

3.4.18 p_0—air pressure in standard conditions (mbar)

3.4.19 T_0—temperature in standard conditions (K)

3.4.20 N_A—Avogadro constant

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[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Background—Signal is caused by contaminations in the sampling system and the ionizer. This is different from the base line signal, which is caused by electronic noise, stray ions, and/or peak tails of very abundant compounds.

[6] In practice this means that a gas mixture can have 20 components present at 10 nL/L (ppb) each. These components shall not produce interfering signals or contribute significantly to the consumption of the reagent ion. Commercially sold ZeroAir cylinders and generators usually guarantee the content to have <0.1 nL/L hydrocarbons. The actual amount of hydrocarbons within a given air needs to be identified separately. In case of the use of a ZeroAir generator, the feedline might require additional scrubbers. Despite of these aspects, a ZeroAir generator is preferred over bottled air for the system blank (see Chapter 12) since the ambient humidity can be an important factor for the calibration in some systems. Zero Nitrogen is an option, with the same conditions as described above.

3.4.21 *l*—length of the ion molecule reactor (m)

3.5 Quantities, their symbols and SI units, non-SI units accepted with the SI and equivalent non-SI units are often used in the scientific literature of this field. In this standard we try to use SI units where possible and indicate scientific jargon units in parenthesis. An overview of the quantities and units used in this field is listed in Table 1.

4. Summary of Test Method

4.1 This method describes the practical aspects of quantification of a proton transfer reaction - mass spectrometer (PTR-MS) in quantifying various volatile organic compounds in ambient air samples. Ambient air samples are drawn through inert tubing and routed to the PTR-MS for analysis. Sampling can be performed either through direct input of the sample gas into the instrument or by using a secondary pump system for sampling from more distant areas by using PTFE, PFA or equivalent sampling tubing; by using the latter approach, distances between sampling spot and instrument of several hundred feet can be achieved. Limitations in terms of distance are described in Sears, et. al. (2013) (3). The inlet can be set up to handle either continuous sampling or for discreet sample intake of previously acquired air samples in, for example, canisters or bags. Instruments configured with a multiport

valve allow different sample flows from discreet, separate locations to be programmatically measured at a single instrument location.

4.2 The instrument is calibrated either from manual input of calibration standards and zero air or through the use of an automated calibration and zero system. Automatic systems are commercially available and can be linked to the PTR-MS through inert tubing. Such systems usually produce zero air for blanks and use a calibration mixture through dynamic dilution of that calibration standard into the zero air. Whether manual or automatic, the concept of calibration remains the same, and is described in detail later in this method.

4.3 This method is used to quantify the concentration of VOCs in the gas phase using ambient air as the carrier gas. In the standard case this method will draw VOCs into the PTR-MS using air as the carrier gas, but gasses that are inert to the method can be substituted as the carrier gas (N_2 or noble gasses). Calibrations and blanks are either conducted automatically using an appropriate calibration system or manually using auxiliary standards.

5. Significance and Use

5.1 Vapor intrusion testing has been performed traditionally using multiple canister samples or thermal desorption tube

TABLE 1 Comparative Listing of SI and Common Units as Applicable to PTR-MS Analyses

Quality	Symbol	SI	non-SI	Comments
Concentration Volumetric Concentration	$C_V{}^V$ $C_N{}^V$	m^3 / m^3	ppmV, ppbV, or pptV	
Mixing Ratio	C			
Number Concentration	$C_V{}^N$	mL^{-1}	$\frac{molecules}{mL}$	
Pressure Independent Gas Flow	F	mL /min hPa L /min	sccm bar mL /min mbar L /min	mL/min is confusing, because it is pressure dependent. It should be called standard mL/min, which is not an SI unit. At the standard pressure of 1.013 bar, all these units are the same.
Mass/charge	m/z		Th = u /e	Th = thomson = $\frac{unified\ atomic\ mass\ unit}{atomic\ charge\ unit}$ =
Mass-to-charge Chargic mass	m/Q M			In PTR-MS, the charge is predominantly +1, therefor m/z is equivalent to the atomic mass unit of the charged molecule.
Signal	S	ions	counts	
Signal intensity, ion count rate	I	Hz ion /s	cps	all three units are common
Sensitivity[A]	s	Hz / (nL /L)	cps/ppb	s = I/C usually in cps/ppb in the literature
Resolving power[B]	R		Th/Th	R = (m/Q)/△(m/Q) is sometimes also referred to as resolution
Resolution	ΔM		Th	ΔM = Δ(m/Q) = the mass difference at which two neighboring peaks can be distinguished
Scan speed	M /t		Th/s	for QMS, which scan the mass range

[A]Sensitivity *s* = signal intensity *I* per concentration *C* of a compound = *I/C*.
[B]Mass resolving power *R* = *M*/Δ*M50%*: for an isolated peak, observed mass divided by the peak width at 50 % height (FWHM, or full-width-at- half-maximum).

samples. These discontinuous measurements have been shown to be snapshots and provide averages of exposure. In many cases a higher temporal resolution is desirable to identify peaks of emissions due to specific occupancy or environmental changes. For these cases, a continuous real-time monitoring solution is desirable. These continuous monitoring setups can be either short-term or be part of a long-term monitoring plan as described in ASTM guide "Standard Guide for the development of LongTerm Monitoring Plans for Vapor Mitigation Systems" (E2600).

5.2 The PTR-MS provides real-time measurement of multiple VOCs at ultra-trace levels, that is, in the µL/L (ppm) to less than pL/L (ppt) range. Its strengths lie with the ability to measure VOCs in real-time and continuously (that is, ~1 Hz or faster, using time-of-flight analyzers), and with limited sample pre-treatment, compared to a gas chromatograph (GC) system, which is commonly the method of choice to measure VOCs using a variety of detectors. In case of PTR-MS with quadrupole analyzers, the terms would be nearreal-time and semi-continuous. The high temporal resolution of the PTR-MS measurement in the range of second(s) is often desired when studying the atmospheric chemistry or source emissions that result in unpredictable, sudden, and short-term fluctuations. For a detailed description on the design and theory and practical aspects of operation for the different types of PTR-MS, please refer to Yuan et al. (2017)(1).

5.3 For ambient air measurements, such as vapor intrusion (VI) related emission testing, the PTR-MS can be used in three different modes of operation: (1) in scanning mode to identify sources and VI entry points within buildings; (2) in variation identification mode, as a continuous monitoring instrument with seconds to minutes of temporal resolution covering a large number of VOCs; (3) in source tracking mode, as a scanner of indoor and outdoor sources and as a rapid tracking device for external emissions; this requires the instrument to be mounted on a moveable platform, such as on an (autonomous) vehicle or trolley. The same operation can be used to identify various other constituents in air, depending on the application—be it fugitive emissions from toxic materials or illicit materials, or metabolic reactions to infections expressed in different breath emissions.

5.4 Spatial and temporal variability are two common challenges with ambient air measurements and source assessments. Within a given building, the sources for vapors can be few or many and are generally irregularly spaced; they may be obscured from view by floor coverings, furniture or walls, which in itself can be a large source of VOC. The current methods of choice require the use of time-discreet monitoring or time-averaged monitoring of a specific sampling spot. Real-time monitoring provides a method to assess the spatial distribution of vapor concentrations, which may help to rapidly and efficiently identify the location of vapor entry points.

5.5 Real time assessment is valuable as a component of a program of assessment with two or more supporting lines of evidence and can be used to:

5.5.1 Provide support for real-time decisions such as where and when to collect long-term samples for fixed laboratory analysis using canisters or sorbent tubes;

5.5.2 Verify data quality (for example, monitoring the efficacy of soil gas probe purging prior to sampling, providing leak checks; and

5.5.3 Measure changes in VOC vapor concentrations in response to changes in building pressure, temperature, solar irradiation, or other weather conditions and factors affecting vapor fate and transport, including secondary chemistry occurring within the building.

5.5.4 Identify alternative pathways based on prior identified intrusion compounds or based on emissions within such pathways, such as stormwater drains.

5.6 Screening of a property prior to a real estate transaction based on site specific potential sources of concern. The option for voluntary investigative assessments of potential VI in the real estate business is described in ASTM method E2600-15.

Note 1—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D3740 are generally considered capable of competent and objective testing/sampling/inspection/etc. Users of this standard are cautioned that compliance with Practice D3740 does not in itself assure reliable results. Reliable results depend on many factors; Practice D3740 provides a means of evaluating some of those factors.

6. PTR-MS Instrument

6.1 This chapter only describes the steps necessary for understanding the quantification of PTR-MS generated data. For general description of the instrument, please refer to Yuan et al. (2017) (1) and Dunne et al. (2018) (2).

6.2 A mass spectrometer is usually considered as consisting of a sampling system, an ionizer, a mass analyzer and data analysis electronics. This is illustrated in Fig. 1.
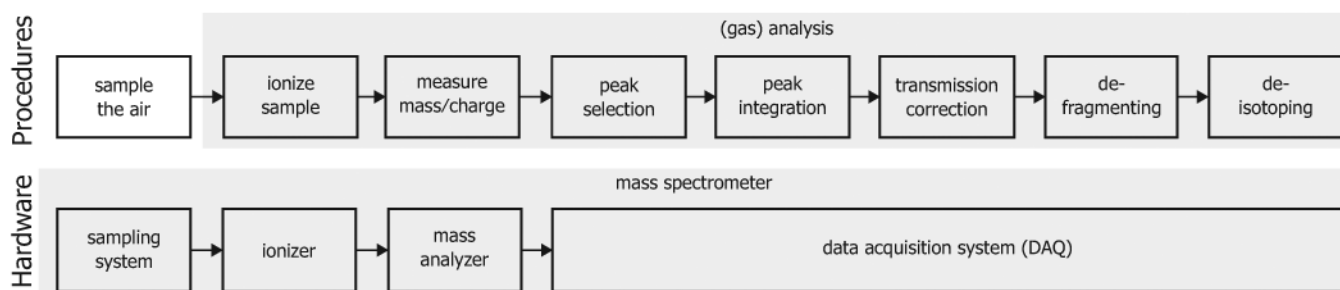

FIG. 1 Definition of Mass Spectrometer (Hardware View) and Analysis (Procedural View) and Their Correspondence

6.3 A gas analysis consists of the following procedures: ionizing the sample gas, mass analysis of the ions, quantifying the mass peaks, correcting for transmission differences of ions with different mass/charge, assigning fragment ions to their parent ions and assigning isotopes to their compound. Those processes are also illustrated in Fig. 1. The last three procedures are not always required. For example, if a measurement of isotope ratios is to be done, the de-isotoping procedure will be omitted.

6.4 Gas sampling is usually done with inert tubes, mostly made of PTFE, PFA, PEEK or equivalent. These tubes are usually temperature controlled. When measuring semi-volatile organic compounds (SVOC) the temperature should be above 100 in order to minimize condensation. It is preferable to keep the sampling lines short and move the mass spectrometer to the sample.

6.5 Chemical ionization (CI) is chosen in this method because it is soft, selective and sensitive.

6.5.1 Soft ionization means that only a small number of fragments are produced from a target compound and a higher likelihood of production of the charged complete molecule. This results in simpler spectra and therefore is key for direct mass spectrometry, for example, analysis without chromatographic separation.

6.5.2 Selective ionization means the main gases (N_2, O_2) of the atmosphere are not ionized. This is important to reach low detection limits. Without selective ionization, the mass spectrometer would be overwhelmed and saturated by the highly abundant air compounds.

6.5.3 Sensitive ionization means that the signal intensity I per concentration C of a compound A is large. This allows for fast measurements and reduces signal-to-noise.

6.6 Chemical ionization means that a compound A is ionized via the chemical reaction with a reagent R. In most cases the reagent is an ion, which is indicated as R^z where z is the charge state of the reagent. In some cases, the reagent can be a neutral, metastable molecule or element, which is indicated as $R^\bullet$.

6.7 The reaction can be of many different types. Common reaction types are proton transfer ionization, electron transfer ionization, or adduct ionization.

6.7.1 PTR-MS uses the reagent ion H_3O^+ and therefore ionizes organic analytes (A) via the following proton transfer reaction:

$$A + H_3O^+ \rightarrow AH^+ + H_2O$$
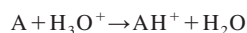
6.7.1.1 Only compounds that have a proton affinity greater than that of water (693 kJ/mol) can be ionized when using the hydronium mode of ionization.

6.7.1.2 This reaction may also take place with water cluster ions $(H_2O)_n H_3O^+$ as reagent ions or adduct ions, which can be helpful in untargeted analytical approaches.

6.7.2 Electron transfer ionization (ETI) can also result in positive ionization:

$$A + R^+ \rightarrow A^+ + R$$
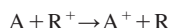
6.7.3 Adduct chemical ionization is sometimes preferred to H_3O^+ because it is even "softer":

$$A + R^+ \rightarrow AR^+$$
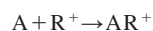
6.7.4 The chemical ionization reaction takes place within the ion molecule reactor (IMR), that is, where the sample air stream interacts with the reagent ions produced by the reagent ion source (Fig. 1). The ion molecule reactor (IMR) is pressure, temperature and voltage adjusted to control reaction kinetics.

6.7.5 The IMR gas pressure determines the reaction dynamics. We differentiate three different pressure regimes:

6.7.5.1 Low pressure chemical ionization (LPCI): $pR < 0.01$ mbar: in this pressure regime, ion molecule reactions are rare. Therefore, secondary reactions are very unlikely. This is the purest form of chemical ionization, but also not very sensitive.

6.7.5.2 Medium pressure chemical ionization (MPCI): 0.01 mbar $< pR < 10$ mbar: in this pressure regime collision energies are sufficiently high to allow disintegrate water clusters; therefore, the medium pressure regime is used for H_3O^+ ionization. However, some secondary reactions do happen, especially with samples of high VOC loads.

6.7.5.3 High pressure chemical ionization (HPCI): 10 mbar $< pR$: In this pressure regime secondary ionization is very likely and the highest sensitivities are achieved since the reaction collisions are very numerous. This is best suited for very clean air measurements.

6.8 Mass analyzers come in different varieties with different properties.

6.8.1 Quadrupole mass analyzers (QMA) are the "traditional" analyzers in PTR-MS. Their resolving power is limited to "unit mass," which means isobars cannot be resolved, which usually is important for CI-MS due to the lack of chromatographic separation. PTR-MS with QMS are ideally deployed when the monitoring duration is over multiple days or weeks and a temporal resolution of multiple minutes is acceptable.

6.8.1.1 *Quadrupole MS*—Analyte ions are measured sequentially in a measurement cycle. In a multiple ion detection cycle the measurement cycle consists of measuring the reagent ion (H_3O^+), other diagnostic ions (O_2^+, NO^+, $(H_2O)_2 H^+$), and up to 50 analyte ions. The instrument repeats this cycle indefinitely storing the data to file.

6.8.1.2 The dwell time (τ) is the length of time the mass spectrometer spends measuring an ion and can be varied to improve signal to noise; typically, dwell time is 1 second for analyte ions. A measurement cycle is the sum of the dwell times of all analytes being measured, which ultimately determines the time resolution of measurements.

6.8.2 Time-of-flight mass analyzers (TOF) have widely replaced the QMA in chemical ionization mass spectrometry. The key differences of TOF-MS instrumentation are the mass resolution[7] of 1 Th (nominal mass) meaning that no elemental composition identification can be performed; and the staggered (nonconcurrent) measurement of individual analyte ions. They can reach high resolving power ($R > 10,000$) which allows separation of many isobars which is very useful to compensate the lack of chromatographic separation. Their high mass

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[7] Mass resolution: $\Delta M50\%$ = peak width at 50% height, which is approximately the smallest difference between two peaks M1 and M2 so that they can be identified as separate signals.

accuracy enables identification of compounds without fragment libraries. They measure all masses simultaneously and therefore are quite sensitive. In addition, they can be quite compact and robust.

6.8.2.1 TOF analyzers require a pulsed and cyclic ion extraction into the field free region of the MS. All ions are measured in each extraction cycle which repeat at a rate of typically 10 to 50 kHz dependent upon instrument specifics. Data from multiple extractions are accumulated into spectra for predefined time periods (typically 0.01 to 10 seconds) to improve signal to noise in the spectra.

6.9 The PTR-MS with TOF analyzers are ideal when rapid changes (bolus events, fugitive emissions) in vapor concentrations are anticipated which require high temporal resolution. Other mass analyzers such as Fourier transform ion cyclotron resonance mass analyzers are used primarily in academic research settings and are not used in field deployments. Data acquisition system (DAQ) usually includes electronics for recording the signals from the mass analyzer and a computing unit.

6.9.1 The recording electronics can be either a time-to-digital converter (TDC) or an analog-to-digital converter (ADC). Whereas TDCs count the ions individually, ADCs measure the current produced by the ions. TDCs are faster, less expensive but have a limited dynamic range. With ADCs becoming faster and mimicking TDC properties, the ADCs gradually replace the TDCs. Modern ADCs have on-board processing, which means some data analysis can be done on-board.

6.9.2 The main processing steps done in the computing unit are listed in Fig. 1:

6.9.2.1 Peak selection can be done in two different ways:
• Peaks are selected from a pre-defined peak list. This is referred to as "targeted analysis."
• Peaks are selected using a peak finder algorithm in addition to the pre-defined peak list or from scratch. This is referred to as "non-targeted analysis."

Many standards include a list of compounds to be measured, which amounts to a "targeted analysis."

In many cases, the "peak finding" of peaks that are not in the peak list is done in post-processing and even manually. The new peaks can then be added to the predefined list and the complete data analysis can be repeated. This blurs the line between targeted and non-targeted analysis.

6.9.2.2 Peak integration collects all signal of an ion species into a single intensity for that species. This process includes mass calibration, integration of a signal peak sometimes using peak fitting, and massspectral baseline correction. These processes can be done either real-time during recording or in postprocessing.

6.9.3 Transmission correction means accounting for the fact that the total ion transmission depends on the mass/charge of an ion. This step does not need to be done when a compound is quantified using a calibration gas with a known concentration of the compound.

6.9.3.1 De-fragmenting means assigning the signal of multiple fragment ions to their precursor ion.

6.9.3.2 De-isotoping means accounting for the mass spectral signal of the various isotopes of a given compound during peak integration, and potentially assigning the integrated signal of less-abundant isotope ions to the monoisotopic ion pertinent to that compound.

6.10 Based on reaction kinetics, the number concentration (in molecules/mL) of neutral VOC [A], in the IMR can be determined by the following equation:

$$[A] = \frac{1}{kt} \frac{I(AH^+)}{I(H_3O^+)} \frac{E(H_3O^+)}{E(AH^+)} \qquad (1)$$

where k is the ion—molecule reaction rate constant (molecules/mL s^{-1}), t is the reaction time (s), $I(AH^+)$ and $I(H_3O^+)$ are the respective ion counts rates (ions/s), and $E(AH^+)$ and $E(H_3O^+)$ are the ion transmission efficiencies through the ion optics and the mass spectrometer. The mixing ratio or concentration of the organic A in the sample air is then determined by the following equation:

$$X(A) = \frac{[A]}{[AIR]_{IMR}} = \frac{[A]}{[AIR]_{IMR}} 10^9 nL/L = \frac{[A]}{[AIR]_{IMR}} 10^9 ppb \qquad (2)$$

where $[AIR]_{IMR}$ is the number concentration of air (molecules/mL) in the IMR; this equation may also be adjusted to take water cluster ion reactions into account.

6.11 In practice the sensitivity of the PTR-MS to various VOCs is determined by using multicomponent compressed gas standards to establish the sensitivity s = I/S (signal intensity per concentration); this sensitivity s is measured in (ions/s)/(nL/L) = cps/ppb.

6.12 In practice, due to differences in ion-molecule reaction rate constant and transmission efficiency, and different degree of fragmentation, different species have different sensitivities. For example, sensitivities are typically larger for polar oxygenated compounds.

7. Special Skills

7.1 This method aims at post-analytical quantification aspects. Personnel must be competent in the operation of the PTR-MS instrument, calibration and blank procedure.

7.2 The user must be educated in the steps to calculate the normalized sensitivity of VOCs using data collected from the PTR-MS and calibration and zero system. Ultimately, this requires the knowledge to determine ambient concentrations of VOCs from the calculated sensitivities. Personnel should also be able to estimate the concentrations of tentatively identified compounds (TIC's) using calculated sensitivities and proton transfer reaction rate constant data.

8. Safety

8.1 Components of the PTR-MS are at a high voltage and protected from accidental human contact. However, care should be taken to avoid contact with energized parts and only qualified PTR-MS technicians should attempt repair or maintenance within potentially energized areas of the instrument.

8.2 The multi-component VOC blend is stored inside a pressurized aluminum bottle with an attached regulator. Before

movement of the bottle from the security straps, the regulator should be removed and the bottle head should be covered with the supplied cap. Safety Data Sheets (SDS) for chemicals, such as analytes and solvents, should be consulted before use. The user of this test method should also be aware of the hazards associated with the operation of the multicomponent VOC blend that contains many toxic compounds. Therefore, the exhaust of the calibration and zero system and PTR-MS should be vented outside the analytical workspace to avoid contamination of the air with the compounds of the multi component VOC mixture. In case of primary ion sources other than hydronium, such as O_2, standard safety procedures are to be consulted for handling gas cylinders with such content.

8.3 Turbomolecular vacuum pumps can fail catastrophically if suddenly exposed to high pressure while they are operating, which could present a hazard to humans or property. Turbomolecular pumps should be turned off and allowed to come to a complete stop before the instrument is vented.

9. Setup, Sample Collection, and Handling

9.1 Fig. 2 illustrates the schematic layout of a basic PTR-MS system. Due to the connection with ZeroAir, a dilution of the actual sample can be performed in case of large amounts of VOC emissions that can overwhelm the instrument. An example could be the investigation of alternative pathways. For calibration the 2-way valve is switched to the calibration gas, while for measurements the valve is switched to the sample inlet side. The sample inlet side can be either a single line of tubing or could be a multi-valve that switches between multiple sampling lines. Due to the relatively low flow rate of the PTR-MS, which is in the range of 100 sccm, it is usually beneficial to use a secondary pump and subsample from that main flow.

9.2 More sophisticated setups have been shown to be adequate for specific problem settings, such as GC-PTR-MS.[8]

9.3 The PTR-MS does not require any pre-conditioning of the sample. While filters can be used to remove larger dust particles, these can also interfere with the vapor content of a sample. A virtual-impactor setup is recommended, in which the PTR-MS samples a small flow orthogonally from a much larger flow supplied by an external pump (see Fig. 2). Depending on the ambient air conditions, some advantages can also be gained through different sampling techniques such as the use of cold traps, nafion dryers, thermal desorption or sample dilution using either a mass flow controller or flow orifices, however, this is not a requirement for general indoor sampling and analyses.

9.4 The sampling line can be extended to the length required by location. Standard tubing diameters in the U.S. are ¼ in. (6.4 mm) or ⅜ in. (9.5 mm) OD; PFA or FEP are materials with a very good (that is, low) retention and price. Sampling lines of up to 100 feet (30.5 m) can be set up.
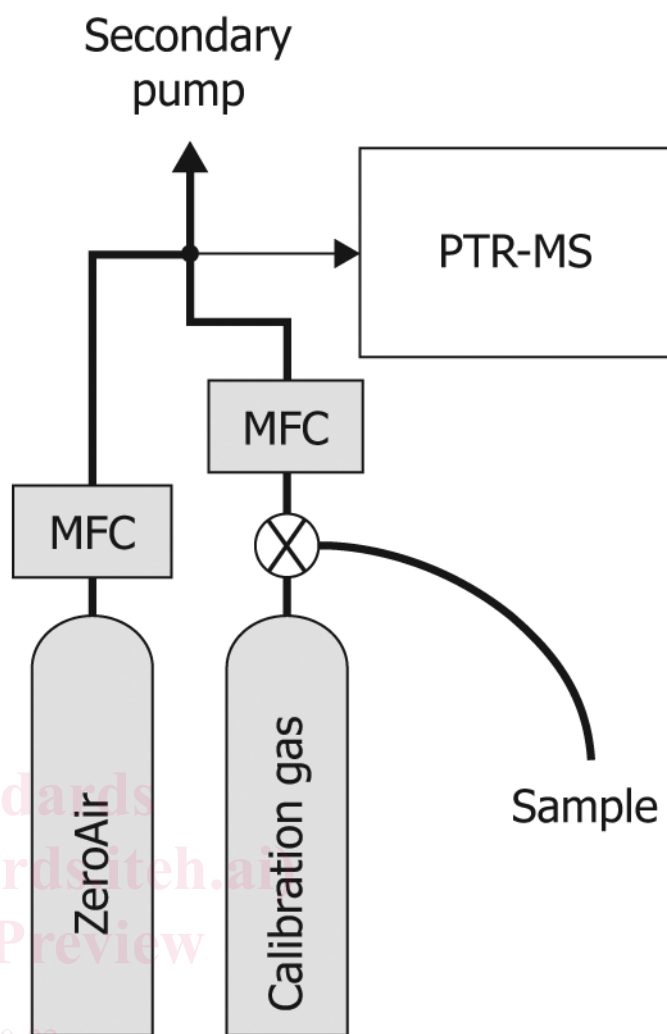

FIG. 2 Basic Configuration of a Calibration and Sampling System for PTR-MS Analysis

9.5 To provide the optimal sample to the instrument guidelines are provided by several ASTM standards, such as, D5314 and D5730. Minimal calibration requirements are shown in Table 2.

9.6 The sampling line is to be kept at a stable temperature into the instrument, ideally with increasing temperature from the point of sampling to the IMR. This avoids the so-called cold spots, which are areas within the sampling line colder than the ambient temperature and which potentially produce false results due to condensation on the walls. However, due to the pressure difference between the ambient pressure and in the IMR, the temperature within the chamber can be reduced up to 20°C in comparison to the inlet tube temperature while still preventing condensation of sampling constituents. This is beneficial to further reduce the amount of fragmentation for labile compounds during ionization.

10. Operating Procedure

10.1 *Startup and Operating Steps*—The individual steps on how to setup a PTR-MS run are highly dependent on the

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[8] Such systems have a reduced ability for real-time monitoring but an additional layer of separation which can be beneficial in tracking very low concentrations of target analytes; a side benefit is that this setup would fulfill the criteria to apply U.S. EPA method 18. For comparison of such methods see Warneke et al. (2015) (4).