Designation: D8460 – 22

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

This standard is issued under the fixed designation D8460; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

[1] This test method is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Groundwater and Vadose Zone Investigations.

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

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction
D5314 Guide for Soil Gas Monitoring in the Vadose Zone (Withdrawn 2015)[4]
D5730 Guide for Site Characterization for Environmental Purposes With Emphasis on Soil, Rock, the Vadose Zone and Groundwater (Withdrawn 2013)[4]
D6026 Practice for Using Significant Digits and Data Records in Geotechnical Data
D8408/D8408M Guide for Development of Long-Term Monitoring Plans for Vapor Mitigation Systems
E2600 Guide for Vapor Encroachment Screening on Property Involved in Real Estate Transactions

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

[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.