Designation: D8455 – 22

Standard Test Method for Speciated Siloxane GC-IMS Analyzer Based On-line for Siloxane and Trimethylsilanol Content of Gaseous Fuels[1]

This standard is issued under the fixed designation D8455; 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 is for the determination of speciated siloxane concentrations in gaseous fuels using on-line Gas Chromatography Ion-Mobility Spectrometry (GC-IMS).

1.2 *Units*—The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.3 *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.*

1.4 *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:*[2]

D3609 Practice for Calibration Techniques Using Permeation Tubes

D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems

D4150 Terminology Relating to Gaseous Fuels

D4298 Guide for Intercomparing Permeation Tubes to Establish Traceability

D5287 Practice for Automatic Sampling of Gaseous Fuels

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6621 Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials

3. Terminology

3.1 *Definitions*—For definitions of terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *siloxanes, n*—a functional group in organosilicon chemical family with the Si—O—Si linkage.

3.2.1.1 *Discussion*—In this test method, "siloxanes" include both "siloxanes and trimethylsilanol (TMSOL)."

3.3 *Abbreviations*—Several of the following abbreviations are for common siloxanes that can be determined according to this test method. This is not meant to construe that this test method is constrained to determining only these substances.

3.3.1 *D3*—Hexamethylcyclotrisiloxane

3.3.2 *D4*—Octamethylcyclotetrasiloxane

3.3.3 *D5*—Decamethylcyclopentasiloxane

3.3.4 *D6*—Dodecamethylcyclohexasiloxane

3.3.5 *DMS*—data management system

3.3.6 *GC-IMS*—Gas Chromatography Ion-Mobility Spectrometry

3.3.7 *L2*—Hexamethyldisiloxane

3.3.8 *L3*—Octamethyltrisiloxane

3.3.9 *L4*—Decamethyltetrasiloxane

3.3.10 *L5*—Dodecamethylpentasiloxane

3.3.11 *NIST*—National Institute of Standards and Technology

3.3.12 *SOP*—standard operating procedure

3.3.13 *TMSOL*—Trimethylsilanol

4. Summary of Test Method

4.1 A representative sample of a gaseous fuel is extracted from a process pipe or pipeline and is transferred in a timely manner through an appropriately designed sampling system to the inlet of a siloxane analyzer. The sample is conditioned with a minimum, preferably negligible, impact on the siloxane content. The line used to transfer gas from the process pipe or pipeline to the instrument is heated to at least 65 °C to prevent condensation of heavier siloxane species. The analyzer sample loop is filled with a known volume of sample gas, after which the contents of this sample loop are injected into a GC-IMS.

[1] This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.12 on On-Line/At-Line Analysis of Gaseous Fuels.

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[2] 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.

Excess process or pipeline sample is either vented to atmosphere, or returned to the process stream, depending on application, safety concerns, and regulatory requirements. If the analyzer is installed inside a building and excess sample gas is vented to atmosphere, the operator should run a ventilation line to a fume hood or outside.

4.2 Sample gas is introduced to a gas chromatographic column, where the various siloxane species and other gas constituents interact with the column material and are separated.

4.3 Siloxanes and other gas constituents elute from the GC column, where they are introduced to the IMS drift chamber. A low-radiation tritium source generates reactant ions $H^+(H_2O)_n$. These reactant ions chemically ionize compounds entering the IMS cell, producing specific analyte ions. These ions are released into the drift chamber at a defined frequency (generally every 30 ms), then forced through the chamber via an applied electric field. Simultaneously, nitrogen gas flows through the drift cell in the opposite direction. As ions are forced against the flow of nitrogen, they are separated by charge and geometry, until they strike a detector at the opposite end of the drift cell. This produces a change in electric potential (analyzer response) proportional to the quantity of ions striking the detector. This two-stage separation produces a 3-dimensional chromatogram, as illustrated in the example below. (See Fig. 1.)

NOTE 1—This illustration is meant for conceptual demonstration of a 3D chromatogram; real chromatograms may include more analyte species (such as TMSOL and D6) as well as non-target compounds.

4.4 A GC-IMS configured to measure siloxanes in gaseous fuels may measure silicon concentration down to the concentrations indicated in Table 1 using a 1 mL sample loop. This is the maximum recommended sample loop volume.

4.5 Calibration, maintenance, quality assurance, and performance protocols provide a means to validate the analyzer operation and the generated results.

4.6 The siloxane species analyzed by the GC-IMS include TMSOL, L2, L3, L4, L5, D3, D4, D5, and D6.

5. Significance and Use

5.1 Combustion of gaseous fuel containing significant siloxane concentrations results in conversion of these siloxanes to silicon dioxide (SiO_2). This SiO_2 accumulates on downstream equipment such as the interior of reciprocating engine cylinders (used for electricity generation and transportation applications), flame sensors, and condenser coils in residential/commercial furnaces, or post-combustion catalysts used for the removal of NO and NO_2. In each of these cases, SiO_2 compromises the performance of the equipment and may lead to eventual failure. Continuous measurement of siloxane concentrations enables a fuel producer to ensure their gas quality meets contractual obligations, regulatory requirements, pipeline injection tariff limits, and internal performance requirements. This method is intended to provide procedures for standardized start-up procedures, operating procedures, and quality assurance practices for on-line analysis of siloxanes using a GC-IMS analyzer.

6. Apparatus

6.1 *Instrument (GC-IMS)*—A gas chromatography column coupled to an ion mobility spectrometer drift cell and electrometer. Table 2 summarizes the recommended analytical parameters for a GC-IMS configured to analyze siloxanes. Some GC-IMS analyzers or configurations may require different settings.

6.1.1 The analyzer is typically configured to log IMS temperature data and flag data as invalid (or prevent the measurement altogether) if temperature is measured outside the acceptable range. The shutter releases ions into the drift cell every 30 ms, during which time the electrometer records the spectrum change in electric potential.

6.2 *Sample Extraction*—The location and orientation of sampling components are critical for ensuring that a representative sample is analyzed. The locations and orientation of sampling components is expected to be selected based upon sound analytic and engineering considerations. Sampling practices for gaseous fuels can be found in Practice D5287. It is of critical importance that the sampling system be heated to at

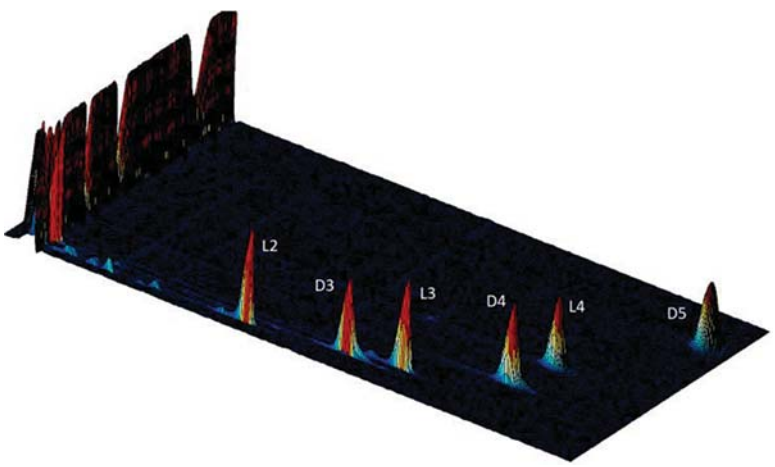

FIG. 1 Conceptual Illustration of a 3D Chromatogram