



Designation: D8455 – 22

# Standard Test Method for Speciated Siloxane GC-IMS Analyzer Based On-line for Siloxane and Trimethylsilanol Content of Gaseous Fuels<sup>1</sup>

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 ( $\epsilon$ ) 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:*<sup>2</sup>

[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.

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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

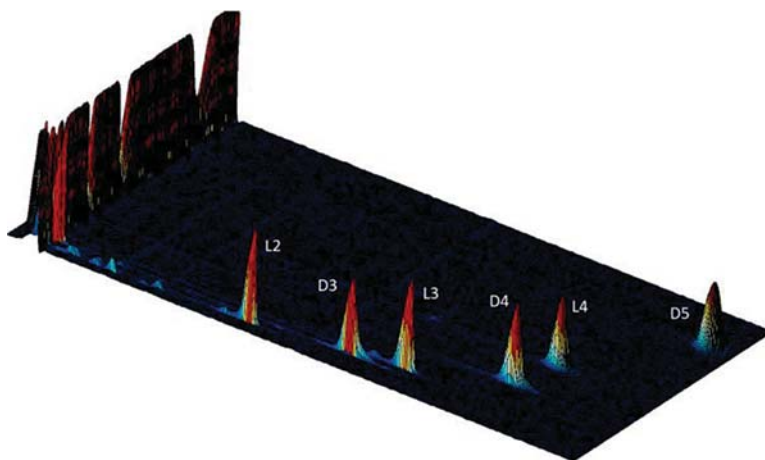


FIG. 1 Conceptual Illustration of a 3D Chromatogram

TABLE 1 Siloxanes Limits of Quantification

| Species                            | Siloxanes and Silanols <i>Limits of Quantification (LOQ)</i> [1 mL Loop] |                       | CAS#      |
|------------------------------------|--|-----------------------|-----------|
|                                    | Silicon (Si)<br>(mg/m <sup>3</sup> )                                     | Silicon (Si)<br>(ppb) |           |
| (TMSOL) Trimethylsilanol           | 0.006  | 1.6                   | 1066-40-6 |
| (L2) Hexamethyldisiloxane          | 0.007  | 1                     | 107-46-0  |
| (L3) Octamethyltrisiloxane         | 0.007  | 0.7                   | 107-51-7  |
| (L4) Decamethyltetrasiloxane       | 0.007  | 0.5                   | 141-62-8  |
| (L5) Dodecamethylpentasiloxane     | 0.018  | 1.1                   | 141-63-9  |
| (D3) Hexamethylcyclotrisiloxane    | 0.008  | 0.9                   | 541-05-9  |
| (D4) Octamethylcyclotetrasiloxane  | 0.008  | 0.7                   | 556-67-2  |
| (D5) Decamethylcyclopentasiloxane  | 0.008  | 0.5                   | 541-02-6  |
| (D6) Dodecamethylcyclohexasiloxane | 0.019  | 1                     | 540-97-64 |

TABLE 2 Recommended GC-IMS Operating Parameters

| Parameter/Component       | Value/Details   |
|---------------------------|---|
| Drift gas flow rate       | 150 mL/min during analysis, 10 mL/min in idle mode                                  |
| Carrier gas flow rate     | 5 mL/min until t=2 min, ramp to 15 mL/min over 30 sec, maintain 15 mL for remainder |
| GC Column temperature     | Isothermal - 80 °C ±0.1 °C  |
| GC Column                 | Low polarity, 30 m length x 0.32 mm ID  |
| Injection                 | Splitless; loop volume varies but 1 mL is suitable for most applications            |
| IMS drift chamber length  | 98 mm   |
| Electrical field strength | 500 V/cm  |
| Scan collection time      | 30 ms   |
| IMS temperature           | 65 °C ±1 °C   |
| Ionization source         | Tritium   |
| Drift chamber pressure    | Atmospheric (1 atm)   |

least 65 °C to prevent condensation of siloxane species, and all sampling system components must be free of silicon-based materials, such as lubricants. Sample gas should be passed through a membrane separator to remove any liquids and solids present in the gas stream before the gas is delivered to the instrument. Excess sample gas may either be returned to the process or vented to atmosphere, dependent on safety concerns and application requirements. If the sample gas pressure exceeds 5 psig, it is recommended that a pressure regulator be installed to reduce the pressure to 5 psig or less.

**6.3 Sample Inlet System**—The siting and installation of an on-line monitor is critical for collecting representative information on siloxanes content. Factors that should be considered in siting an instrument include ease of access for repair or maintenance, sample uniformity at the sampling point, appropriateness of samples from a sampling location, ambient conditions, and of course safety issues. All sampling system components in contact with the fuel stream must be constructed of inert and organosilicon-free materials. Care should be taken to ensure that the extracted sample is maintained as a particulate and condensate free gas, which can be accomplished with the use of an appropriately selected membrane filter. Heat tracing along the sample line to the analyzer is required to ensure that higher molecular weight siloxane species are kept in the gas phase. If a membrane filter is included in the sampling system, or any other components between the sampling connection and the analyzer inlet, they must also be heated. It is recommended that all heated components maintain a temperature of at least 65 °C. Sample gas should be brought to the analyzer continuously and conveyed through a bypass loop that either vents to atmosphere or is returned to the source gas pipe. If venting to atmosphere, an appropriately designed scrubber or control device may be used. Although sample gas

is delivered to the analyzer continuously, the analyzer only withdraws a small subsample of the gas immediately before a measurement begins. This subsample is delivered to the GC column through a sample loop with a known volume. The volume selected for the sample loop is based on application requirements and expected concentrations of siloxane species. The sampling frequency relative to the process bandwidth is critical to ensuring that the reported analytical results adequately represent the process being monitored. The Nyquist-Shannon sampling criterion of a sampling frequency that exceeds twice the process bandwidth can be used to establish a minimum analytical cycle time.<sup>3,4</sup> Typical measurement frequency is 2-3 times per day, but measurements may be acquired up to once per hour.

**6.3.1 Carrier and Drift Gas Control**—Constant flow control of carrier and IMS drift gases is critical for optimum and consistent analytical performance. For the specific GC-IMS analyzer described in this method, ultra-high-purity nitrogen is used for both carrier gas and IMS drift gas. Flow rates and pressures are maintained by use of electronic pressure controllers. Depending on the application and site-specific requirements, rotameters may be used to control gas flow downstream of the analyzer, whether the gas is being directed back to the source pipe or is vented to atmosphere. Plumbing should be designed to ensure the pressure of gas within the analyzer’s sample loop is as close to one atmosphere pressure as possible. Temperature control is vital for ensuring consistent operation of the instrument. Carrier/Drift gas pressure must not exceed 6 bar(600 kPa) at the inlet to the analyzer. (See Fig. 2.)

<sup>3</sup> Nyquist, H., “Certain Topics in Telegraph Transmission Theory,” *Trans. AIEE*, Vol 47, Apr. 1928, pp. 617-644.

<sup>4</sup> Shannon, C. E., “Communication in the Presence of Noise,” *Proc. Institute of Radio Engineers*, Vol 37, No. 1, Jan. 1949, pp. 10-21.

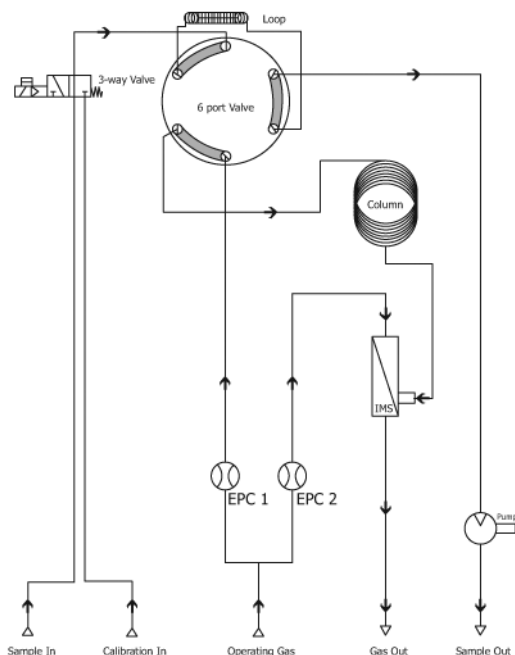


FIG. 2 GC-IMS Siloxane Analyzer Flow Diagram

6.3.2 *Detector*—The GC-IMS detector is an electrometer, which measures a change in electric potential when ionized siloxanes (or any other compounds susceptible to ionization through the tritium-hydronium pathway) pass through the IMS drift cell and strike the detector. The magnitude of induced electric potential is proportional to the number of ions (and therefore concentration of the analyte) striking the detector at any given moment in time. The correlation between ion concentration and change in potential is non-linear, and therefore any calibration curve generated will necessarily also be non-linear. GC-IMS calibrations for this application typically utilize a Boltzmann curve fit, where peak height is used as the dependent variable. Calibration curves are created for each species measured, and should include a minimum of five concentration levels spanning the full calibration range. Calibration ranges are given in Table 3.

NOTE 2—Lower limits may vary by instrument and smaller sample loop volumes may be used to increase the upper limits of calibration ranges.

6.4 *Data Acquisition*—Following a measurement, the GC-IMS analyzer produces a measurement file and a report. The measurement file contains data related to analyzer conditions during the measurement, such as temperatures, electronic pressure controller pressures and flow rates, as well as sample duration. The measurement file also includes the complete three-dimensional chromatographic data for the analysis (the three axes being signal current, IMS drift time, and GC

retention time). The report includes essential information such as device ID, timestamp, and the name of the associated measurement file. The report also includes concentration data for each individual measured species, as well as the total siloxane concentration, the total SiO<sub>2</sub> concentration, and the total Si concentration (the latter two are mathematically derived from the total siloxane concentration, as explained in 11.1).

6.4.1 Data is typically stored locally on the GC-IMS computer, but it may also be retrieved via USB connection. The analyzer may also be configured to automatically send data via communication with a TFTP server to a data management system (DMS), or an operator may retrieve data from a remote location via SSH connection.

## 7. Reagents and Materials

**Warning**—Compressed gas cylinders should only be handled in well ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders can result in explosion. Rapid release of nitrogen can result in asphyxiation.

7.1 *Standards*—Accurate siloxane standards are required for the accurate calibration of GC-IMS analyzers. Calibration may be performed either with permeation tubes or a calibration gas delivery apparatus. All standards shall have a certified concentration traceable to NIST or similar standard reference material source.

7.2 *Prepared Standards*—Compressed gas standards should be stable as defined by the manufacturer’s certification, of the highest available accuracy and purity and used in accordance with the manufacturer’s recommendations. The matrix components in the reference standard are ideally representative of the monitored gas. Alternatively, a simplified matrix can be used if

TABLE 3 Typical GC-IMS Calibration Ranges

| Typical GC-IMS Calibration Ranges; 1 mL Sample Loop |                            |
|---|----------------------------|
| Species   | Range (mg/m <sup>3</sup> ) |
| TMSOL   | 0.03-1.5                   |
| L2,L3,L4,D3,D4                                      | 0.02-1.5                   |
| D5,L5   | 0.05-4.5                   |
| D6  | 0.1-9.0                    |