Designation: D8230 – 19

Standard Test Method for Measurement of Volatile Silicon-Containing Compounds in a Gaseous Fuel Sample Using Gas Chromatography with Spectroscopic Detection[1]

This standard is issued under the fixed designation D8230; 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 primarily for gas-phase siloxane compounds present in biogas and other gaseous fuel samples at ppmv and high ppbv concentrations. It may also be applicable to low ppbv concentrations under certain circumstances.

1.2 *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.*

1.3 *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]

D4150 Terminology Relating to Gaseous Fuels

2.2 *Government Documents:*

Compendium Method TO-15 Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)[3]

NIOSH Manual of Analytical Methods (NMAM) - 4th Edition Development and Evaluation of Methods[4]

3. Terminology

3.1 *Definitions*—For definitions of general gaseous fuel terms used in this test method, refer to Terminology D4150.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical sequence, n*—describes how and the order that field and QC samples in an analytical batch are analyzed.

3.2.2 *calibration standard (ICAL), n*—a mixture of an analyte at a known concentration prepared from a primary stock.

3.2.2.1 *Discussion*—A calibration standard is analyzed at varying concentrations and used to calibrate the response of the measurement system with respect to analyte concentration.

3.2.3 *Continuing Calibration Verification (CCV) Standard, n*—a solution (or set of solutions) of known analyte concentration used to verify freedom from excessive instrumental drift; the concentration is to be near the mid-range of a linear calibration curve.

3.2.4 *gas phase sample, n*—a direct-injection sample that has been collected in a device such as a summa canister or Tedlar bag.

3.2.5 *Initial (or Independent) Calibration Verification (ICV) Standard, n*—a solution (or set of solutions) of known analyte concentration used to verify calibration standard levels; the concentration of analyte is to be near the mid-range of the calibration curve that is made from a stock solution having a different manufacturer or manufacturer lot identification than the calibration standards.

3.2.6 *integration filter, n*—a mathematical operation performed on an absorbance spectrum for the purpose of converting the spectrum to a single-valued response suitable for representation in a two-dimensional chromatogram plot.

3.2.7 *internal standard, n*—a non-analyte element, present in all calibration, blank, and sample solutions, the signal from which is used to correct for non-spectral interference or improve analytical precision.

3.2.8 *laboratory control sample (LCS), n*—a laboratory control sample is an analyte-free matrix to which a known quantity of analyte is added.

3.2.8.1 *Discussion*—The LCS is subjected to the same

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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.

[3] Available from U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Durham, NC 27709, https://www.epa.gov.

[4] Available from The National Institute for Occupational Safety and Health (NIOSH), https://www.cdc.gov.

processing as field samples and is carried through the entire analytical process. The percent recovery of the analytes in the LCS is used to assess method performance. Certain programs and projects require analysis of a duplicate laboratory control sample (LCSD).

3.2.9 *library reference spectrum, n*—an absorbance spectrum representation of a molecular species stored in a library database and used for identification of a compound/compound class or deconvolution of multiple co-eluting compounds.

3.2.10 *method blank (MB), n*—an analyte-free matrix which is processed and carried through the entire analytical process. It is used to evaluate the process for contamination from the laboratory.

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

3.2.12 *sorbent tube sample, n*—a sample that contains solid sorbent and requires extraction prior to analysis.

4. Summary of Test Method

4.1 This test method is used to determine the gas-phase concentrations of selected volatile silicon compounds in the ppbv to ppmv concentration range in biogas and other gaseous fuel samples where gas chromatography is used to speciate the target analytes. A spectroscopic detection method is then used to detect and quantify the silicon compounds. Volatile silicon compounds analyzed according to this method include trimethylsilanol, hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethyltrisiloxane, octamethylcyclotetrasiloxane, decamethyltetrasiloxane, decamethylcyclopentasiloxane, dodecamethylpentasiloxane, and dodecamethylcyclohexasiloxane. Additional compounds may be analyzed provided the data satisfies data quality objectives specified in this standard.

5. Significance and Use

5.1 Silica generated from the combustion of gases containing siloxane compounds can damage internal combustion engines or microturbine blades, reduce heat transfer efficiency of landfill gas and biogas equipment, and poison catalytic oxidizers that are used to control regulated volatile organic compound emissions. The ability to analyze siloxanes in biologically derived fuel gases and other gaseous fuel matrices is highly desirable in order to assess the initial siloxane content and the efficacy of gas pretreatment measures.

6. General Interferences

6.1 *Gas Phase Samples*

6.1.1 *Highly Reactive Matrices*—Certain highly reactive matrices have the capability to damage the passivated surface of a sample canister.

6.1.2 *High Humidity Matrices*—Sample streams at elevated temperatures that contain high concentrations of water vapor may condense water in a sample canister. Condensed water may absorb or react, or both, with some target analytes.

6.1.3 *Valve Lubrication*—Any equipment utilizing a valve may have lubrication that contributes unknown quantities of siloxanes depending on brand and construction materials.

6.1.4 *Stainless Steel Canisters*—Less volatile siloxanes may adhere to stainless steel or nickel surfaces.

6.1.5 *Gas Sampling Bags*—Less volatile siloxanes may adhere to the inner surface of sampling bags resulting in low analytic recoveries for these components.

6.2 *Sorbent Tubes*

6.2.1 *High Humidity Matrices*—Sample streams at elevated temperatures that contain high concentrations of water vapor may condense water at the inlet end of sorbent tubes. Condensed water may cause clogging or irregular sample flow through sorbent tubes.

6.2.2 *Solvent Effect*—Standards prepared in a solvent may show chromatographic distortions and retention time variation due to the high solvent vapor concentrations.

6.2.3 *Sample Preparation*—Interferences due to contaminants in sorbents, solvents, reagents, glassware, and other sample processing hardware can result in artifacts or elevated baselines, or both, in detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of analysis. All glassware associated with this method must be scrupulously cleaned to avoid contamination.

6.3 *Instrument Interferences*

6.3.1 *Matrix Effect*—Samples with a high hydrocarbon content may attenuate the spectral signal; hence, it may be necessary to use the lowest volume possible to meet detection limit requirements when analyzing some biogases. Each spectral detector should be evaluated for their optimal analyte range and hydrocarbon interference.

6.3.2 *Gas Chromatograph*

6.3.2.1 *Column Bleed*—Films made of dimethyl polysiloxane can break down to give column bleed, at higher temperatures. Using a lower bleed column such as diphenyl dimethyl polysiloxane or 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane reduces column bleed.

6.3.3 *Mass Spectrometer (MS)*

6.3.3.1 Tune the MS as needed in order to obtain consistent and acceptable performance.

6.3.3.2 MS source cleaning and other maintenance should be performed as needed depending on the performance of the unit.

6.3.4 *Inductively Coupled Mass Spectrometer (ICP-MS)*

6.3.4.1 Siloxanes are stable and generally do not react quickly with most sample matrices. The mass abundance ratio of silicon is unique and easily identifiable.

6.3.4.2 *Spectroscopic Interferences*—Polyatomic interferences are caused by polyatomic ions that are formed from ions that originate in the sample matrix, reagents used for preparation, and plasma gases. Interfering ions carry a mass to charge ratio that is identical to that of the analyte ion. Polyatomic interferences are minimized with the use of collision/reaction gas in a collision/reaction cell. Silicon has isotopes with masses 28, 29, and 30. Table 1 shows possible interferences with these masses. The isotopes in bold face indicate that it is the most abundant isotope for that element.

6.3.5 *Atomic Emissions Detector (AED)*

6.3.5.1 Silicon emissions are measured at a wavelength of 251.6 nm or 221.7 nm. High concentrations of carbon from co-eluting hydrocarbons can result in a false positive interference for siloxane at its measured wavelength. Typically the

TABLE 1 Polyatomic Interferences with Silicon in ICP-MS

Silicon Isotope	Interference
^{28}Si	$^{14}N_2^+$, $^{12}C^{16}O^+$
^{29}Si	$^{14}N_2{}^1H^+$, $^{14}N^{15}N^+$, $^{12}C^{16}O^1H^+$, $^{12}C^{17}O^+$, $^{13}C^{16}O^+$, $^{28}Si^1H^+$
^{30}Si	$^{14}N_2{}^1H_2^+$, $^{14}N^{15}N^1H^+$, $^{15}N_2^+$, $^{14}N^{16}O^+$, $^{12}C^{18}O^+$, $^{13}C^{17}O^+$, $^{13}C^{16}O^1H^+$, $^{12}C^{17}O^1H^+$, $^{12}C^{16}O^1H_2^+$, $^{29}Si^1H^+$

selectivity of silicon to carbon is near 30 000:1. Carbon concentration can be monitored simultaneously with silicon by measuring the carbon wavelength at 247.9 nm (for 251.6 nm Si) or 193.1 nm (for 221.7 nm Si). This data, along with viewing the raw spectral data in the 251.6 nm range, can be used to identify carbon interference. Silicon emits as a 'triplet' with minor emission bands at 250.7 nm and 252.9 nm in addition to the measured emission band at 251.6 nm. If using 221.7 nm, a similar 'triplet' is observed with additional bands at 220.8 nm and 221.2 nm. These 'triplets' form a unique 'fingerprint' signal for silicon. When a high concentration of carbon is present, a series of minor emission bands will appear in addition to the strong emission at 247.9 nm or 193.1 nm. One of these minor emission bands can overlap with the measured silicon emission and result in a false positive. Therefore a positive signal without the silicon triplet 'fingerprint,' in addition to a strong carbon emission at 247.9 nm or 193.1 nm, suggests carbon interference.

7. Apparatus

7.1 *Sample Collection Apparatus*

7.1.1 *Passivated Stainless Steel Canisters*—Clean, evacuated stainless steel containers whose surfaces have been passivated with a fused-silica lining. May be used to collect grab samples, or attached to flow regulator for collection of composite samples.

7.1.2 *Gas Sampling Bags*—Clean sample bags made of non-reactive and non-absorbing material, such as Tedlar, which includes a sampling valve with septum. Note that for some detectors, the valve must be free of silicone grease. High molecular weight siloxanes may have adsorption issues with these type sample containers. These sample containers may be used to collect grab samples, or attached to flow regulator and pump, if necessary, for collection of composite samples.

7.1.3 *Sorbent Tubes*—Hydrophobic carbon-based sorbents such as Anasorb 747 sorbent have been successfully interfaced in a 500 mg⁄250 mg dual bed, packed into an SPE reservoir, outfitted with two frits (NMAM - 4th Edition). Alternative sorbents may be used provided they meet the desorption efficiency study criteria specified in Appendix X1.

7.2 *Instrumentation*

7.2.1 *Preconcentration System*—Preconcentration may be used to remove water vapor and matrix gases from the gas sample. Method parameters are optimized to separate sample matrices and for maximum analyte recoveries.

7.2.2 *Gas Chromatograph*—A gas chromatograph with or without cryogenic focus will be interfaced to a spectral detection system. A low to mid-polarity column will give separation of siloxanes and other volatile silicon compounds.

7.2.3 *Detectors*—Many different types of detectors may be used for identification and detection of siloxanes and other volatile compounds; this includes but is not limited to: mass spectrometer (MS), inductively coupled plasma-mass spectrometer (ICP-MS), or atomic emissions detector (AED). As long as the detector meets the performance criteria in this method for each compound of interest it may be utilized.

8. Reagents and Materials

8.1 *Reagents for Sample Preparation*

8.1.1 Samples collected in canisters may be pressurized with dry UHP nitrogen. Most biogas samples are humid; in the case of dry samples, humidity may be added to improve recoveries of siloxanes from canisters.

8.2 *Instrumentation Gases*—Gas requirements depend on instrumentation being used, but use of UHP grade gases is suggested.

8.3 *Internal Standards*—The internal standard mixture used for siloxanes analysis depends on the instrumentation being used. For example, GC-MS instruments will use a VOC analysis internal standard mixture, such that it does not interfere with the target analytes and is not routinely prevalent in the matrix. Such examples include bromofluorbenzene, diethylene glycol dimethyl ether. If using a GC-ICP-MS, a mixture of brominated compounds is preferable for use as internal standards.

8.4 *Siloxanes Standards*

8.4.1 It is desirable that two sources of siloxanes standards are utilized for calibration and QA purposes. The standards may be purchased in cylinders or neat form, or prepared in the laboratory.

8.4.2 *Liquid Phase Neat Standards*—Laboratory-prepared standards will require the purchase of neat standards. Purities range from 97.0 % to 99.5 %.

8.4.3 Liquid phase standards are prepared and stored in a refrigerator at or below 4 °C, and protected from light.

8.4.4 Purchased standards are replaced after 5 years or as recommended by the manufacturer.

8.4.5 Stock standards may be prepared in either n-Hexane (99.5 % or equivalent), or methylene chloride (gas chromatography grade, or equivalent).

8.4.6 *Gas Phase Static Dilution*

8.4.6.1 n-Hexane, (99.5 %), or equivalent. "Hexane" containing a mixture of hexane isomers should not be used as some isomers may co-elute with target analytes and interfere with the analyte quantitation masses.

8.4.6.2 Inject an aliquot of the liquid stock standard into a canister while pressurizing with nitrogen. The injection point must be heated to avoid condensation and adsorption loss of siloxanes at the injection site. Continue to dilute with nitrogen until the desired concentration has been achieved.

9. Hazards

9.1 Standard procedures for the safe handling of flammables, compressed gases, and cryogenic fluids should be followed.

9.2 Safety considerations specific to apparatus or instrumentation fluids should be followed.

10. Sampling and Sample Preparation

10.1 *Section A: Gas Phase Sample Collection*

10.1.1 *Tedlar Bags*—If sampling from a positive pressure source, the bag can be filled to 60 to 75 % of capacity. If sampling from ambient or sub ambient sources, a lung sampler or related type of vacuum chamber can be used to fill the bag.

10.1.2 *Sample Handling and Preservation*

10.1.2.1 *Summa Canisters*—If necessary, pressurize the canister to the desired pressure (maximum 40 psig, or 2828 Torr).

10.1.2.2 *Tedlar Bags*—Studies have shown siloxane recoveries to quickly degrade in Tedlar Bags.[5,6,7] It is recommended that samples are analyzed within 72 h of sampling (Compendium Method TO-15). The valve of the bag should be inspected for possible leaks, and it is recommended that bags are stored in a dark, cool environment.

10.2 *Section B: Sorbent Tube Sample Collection*

10.2.1 The recommended sampling rate is 0.2 L/min to 1.0 L/min for a total sample volume of 30 L. Different sampling volumes may be used depending on sampling application. If samples are taken from a positive pressure source, tubes can be connected to a rotameter or dry test meter on the outlet end to measure flow. If the samples are taken at ambient or negative pressure, a sample pump may be used.

10.3 *Sample Handling and Preservation*

10.3.1 Thermal preservation is not required for the SPE cartridges prior to shipment to the field, after field sampling, in transit to the laboratory or once received in the laboratory. The samples, extracts, media, and standards must all be stored separately to minimize contamination. The hold time should not exceed 14 days. The hold time from extraction to analysis should not exceed 30 days.

10.3.2 *Sample Extraction Prior to Analysis*—In a hood, remove the end caps. Decant the two sections of sorbent into two separate clean vials. Add 3 mL of methylene chloride to each vial and agitate vials. Allow the vials to sit for a minimum of 30 min with periodic agitation. Take an aliquot of the extract, transfer it to a 2 mL autosampler vial (or equivalent), and add internal standard.

11. Equipment Preparation

11.1 Place all equipment in service and in accordance with the manufacturer's instructions. Since there are many options, as long as the equipment utilized meets the quality control performance criteria as listed in this method, it may be utilized at the laboratory's discretion.

11.2 *Column Conditioning*—Initial conditioning of the chromatographic column is required prior to use. The column should be conditioned with a continuous flow of helium (UHP/ZERO 99.999 % purity or better) and GC temperature ramp programmed from 40 °C to 250 °C at a rate of five degrees per minute. The column should then be held at 250 °C for 2 h.

11.3 *Instrument Performance Check*—Performance checks should be completed before initial startup and after every 24 h period of operation.

11.3.1 *GC-MS*—The GC-MS system must meet the mass spectra ion abundance criteria for bromofluorobenzene. Refer to instrument manufacturer tuning criteria.

11.3.2 *GC-ICP-MS*—The system is optimized manually based on the instrument response to 10-ppm xenon in helium. Torch position and lens voltages are adjusted to give the maximum signal for Xe-128 and Xe-132. The pulse/analog (P/A) factor must be tuned after the sensitivity tune. The quadropole and electromultiplier detector are tuned if there has been an obvious change in sensitivity or when a new calibration will be prepared. This is accomplished by performing the E/M tuning and Resolution/Axis tuning. The P/A factor is set to 1 during E/M tuning, so the P/A factor must be tuned directly after the E/M tuning is performed.

11.3.3 *GC-AED*—Alignment of the AED is automated by the instrument upon startup. Realignment should be performed after every 24 h period of operation.

11.4 *Initial Calibration Curve*

11.4.1 *Percent Relative Standard Deviation of the Relative Response Factor (%RSD RRF)*—The %RSD RRF for each siloxane component in the initial calibration must be less than 30 % for the calibration to be considered valid for that component. The %RSD RRF is calculated for each siloxane component in the calibration according to Eq 13.

11.4.2 *Correlation Coefficient*—Alternatively, if the RRF cannot meet the 30 % criteria, the absolute value of the correlation coefficient must be calculated for each compound. This value must be at least 0.990 to be valid.

11.4.3 To determine the validity of the continuing calibration curve, a mid-level CCV is analyzed with each batch of 10 samples, or daily. If the calibration check-standard fails to meet QA requirements, another CCV is run to verify the failure. If the CCV fails QA on the second run, then a new multi-point calibration curve must be prepared or other corrective action taken and documented, or both.

11.4.4 *Internal Standard Area Response*—The area response of each quantitation internal standard at each calibration level must be within ±50 % of the mean response of the initial calibration runs.

11.4.5 *Relative Retention Times (RRT)*—The relative retention time (RRT) for a target compound is defined as the retention time of the target compound divided by the retention time of the internal standard, as shown in the following equation:

$$RRT = \frac{RT_i}{RT_{IS}} \quad (1)$$

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[5] Arrhenius, K., et.al., "Suitability of Vessels and Adsorbents for the Short-term Storage of Biogas/Biomethane for the Determination of Impurities – Siloxanes, Sulfur Compounds, Halogenated Hydrocarbons, BTEX," *Biomass and Bioenergy*, Vol 105, 2017, pp. 127-135.

[6] Eichler, C., et. al.,"Evaluation of Sampling Techniques for Gas-phase Siloxanes in Biogas," *Biomass and Bioenergy*, Vol 108, 2018, pp. 1–6.

[7] Bora, R., et. al., "Development of a Universal Analytical Technique for Determining Siloxane Content in Biomethane," *Operations Technology Development Project 7.16.g*, 2018.