

RNG WORKS



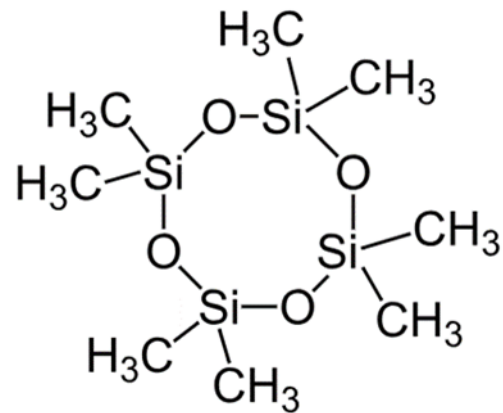
ASTM D8230-19

The first standardized testing Method for Siloxanes in RNG

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OVERVIEW

- ▶ History and background
 - ▶ ASTM International
 - ▶ D03 Committee on Gaseous Fuels
 - ▶ WK 52796
- ▶ ASTM D8230-19
 - ▶ Components covered
 - ▶ Sampling techniques
 - ▶ Instrumentation
 - ▶ Calibration requirements
 - ▶ QA/QC requirements
- ▶ Next steps



ASTM International

- ▶ 1898 - American section of IATM
 - ▶ Members formed by producers and users
 - ▶ From its inception, apparent that Standards would require periodic modification
- ▶ 1902 - Split with IATM and renamed American Society for Testing Materials
 - ▶ Did not want to limit membership
 - ▶ Resisted European practices of government standard bureaus in favor of voluntary standards development
- ▶ 2001 - Becomes international organization



ASTM Committee D03 on Gaseous Fuels

- ▶ Formed in 1935
- ▶ 204 Members (Dec 2019)
 - ▶ 50% Producers
 - ▶ 33% Users / Consumers
 - ▶ 17% General Interest
- ▶ Liaisons from other organizations
 - ▶ AGA
 - ▶ CEN
 - ▶ ISO

D03.01 Collection and Measurement of Gaseous Samples

D03.03 Determination of Heating Value and Relative Density of Gaseous Fuels

D03.05 Determination of Special Constituents of Gaseous Fuels

D03.07 Analysis of Chemical Composition of Gaseous Fuels

D03.08 Thermophysical Properties

D03.12 On-Line/At-Line Analysis of Gaseous Fuels

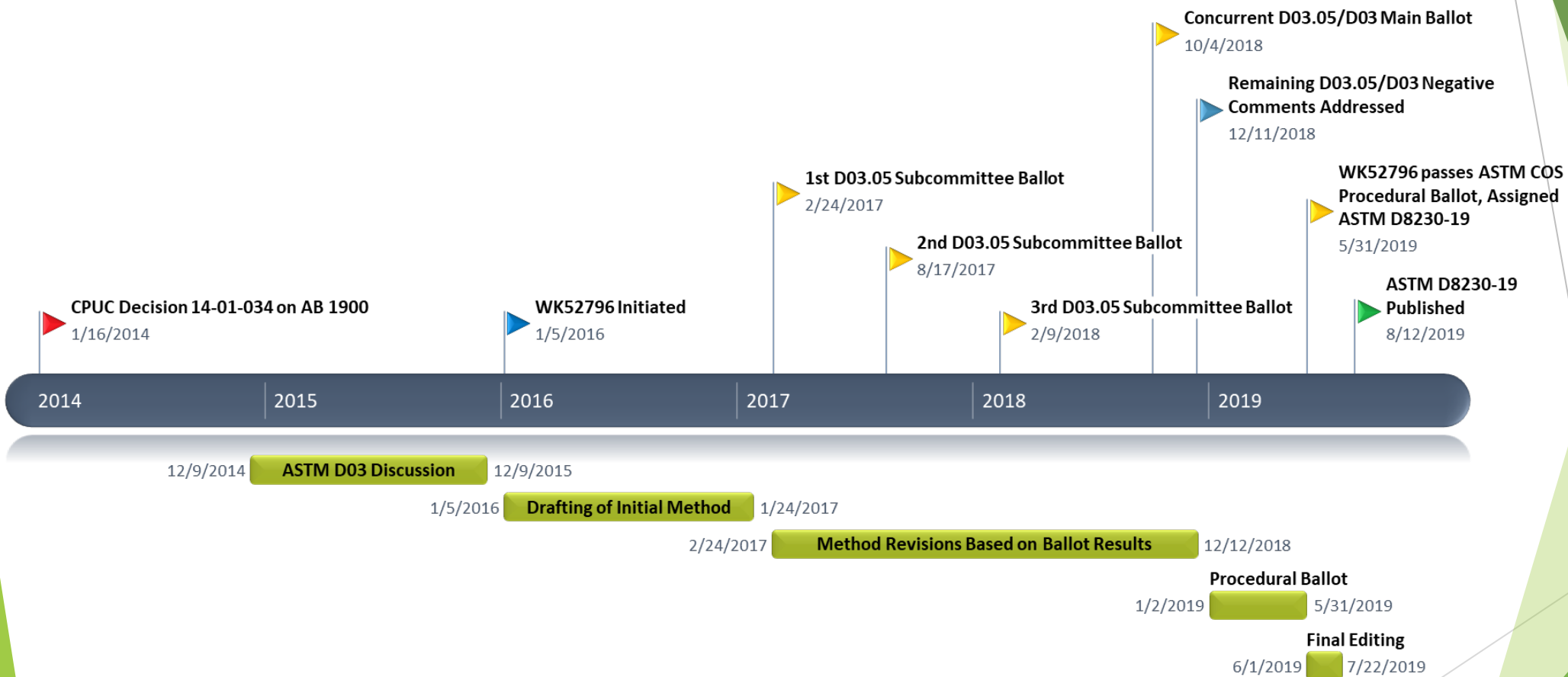
D03.14 Hydrogen and Fuel Cells

Why the need for a published standard?

- ▶ Driven by regulation
 - ▶ CA limits established in 2014 - no referenced methodology
- ▶ Variations to 'in-house' methods developed by individual laboratories
 - ▶ Sampling media and techniques
 - ▶ Analytical instrumentation
 - ▶ Target analytes (or lack of speciation)
 - ▶ Reporting units
 - ▶ Quality control requirements
 - ▶ The intention of the ASTM method is to align laboratory techniques for comparative purposes between labs



WK52796 to D8230-19 Timeline



ASTM WK52796 Becomes D8230-19

Standard Test Method for Measurement of Volatile Silicon-Containing Compounds in a Gaseous Fuel Sample Using Gas Chromatography with Spectroscopic Detection
- Published August 2019



ASTM D8230-19: Minimum Components

Component	CAS #	Acronyms
Trimethylsilanol	1066-40-6	TMS, MOH
Hexamethyldisiloxane	107-46-0	L ₂ , MM
Hexamethylcyclotrisiloxane	541-05-9	D ₃
Octamethyltrisiloxane	107-51-7	L ₃ , MDM
Octamethylcyclotetrasiloxane	556-67-2	D ₄
Decamethyltetrasiloxane	141-62-8	L ₄ , MD ₂ M
Decamethylcyclopentasiloxane	541-02-6	D ₅
Dodecamethylpentasiloxane	141-63-9	L ₅ , MD ₃ M
Dodecamethylcyclohexasiloxane	540-97-6	D ₆

ASTM D8230-19: Sample Collection

Gas Phase Sample Collection

- ▶ Stainless steel containers whose surfaces have been passivated with a fused-silica lining
 - ▶ 14 day hold time
- ▶ Sample Bags made of non-reactive and non-absorbing material, such as Tedlar®
 - ▶ 72 hour hold time



ASTM D8230-19: Sample Collection

Sorbent Tube Sample Collection

- ▶ Hydrophobic carbon-based sorbents
 - ▶ 500 mg / 250 mg dual bed
 - ▶ 0.2 L/min recommended sampling rate
 - ▶ 30 Liter recommended sampling volume
 - ▶ Solvent extraction
 - ▶ Hold times
 - ▶ 14 days from sampling to extraction
 - ▶ 30 days from extraction to analysis

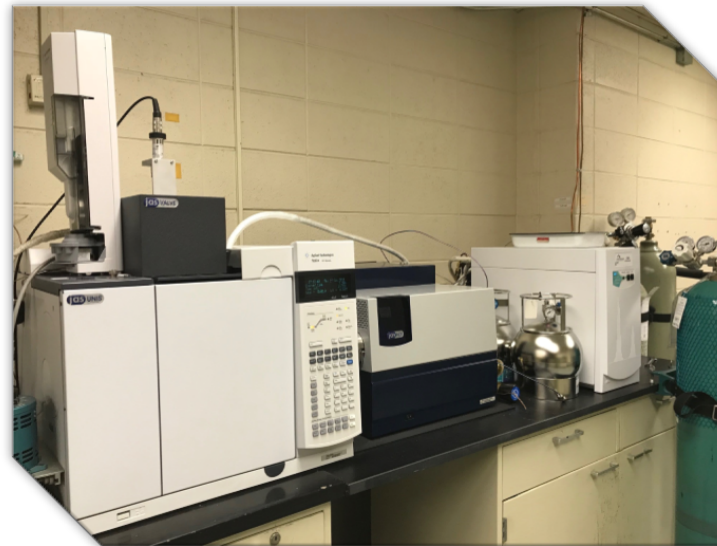


ASTM D8230-19: Instrumentation

Gas Chromatography coupled with Spectroscopic Detector



Mass Spectrometry (GC-MS)

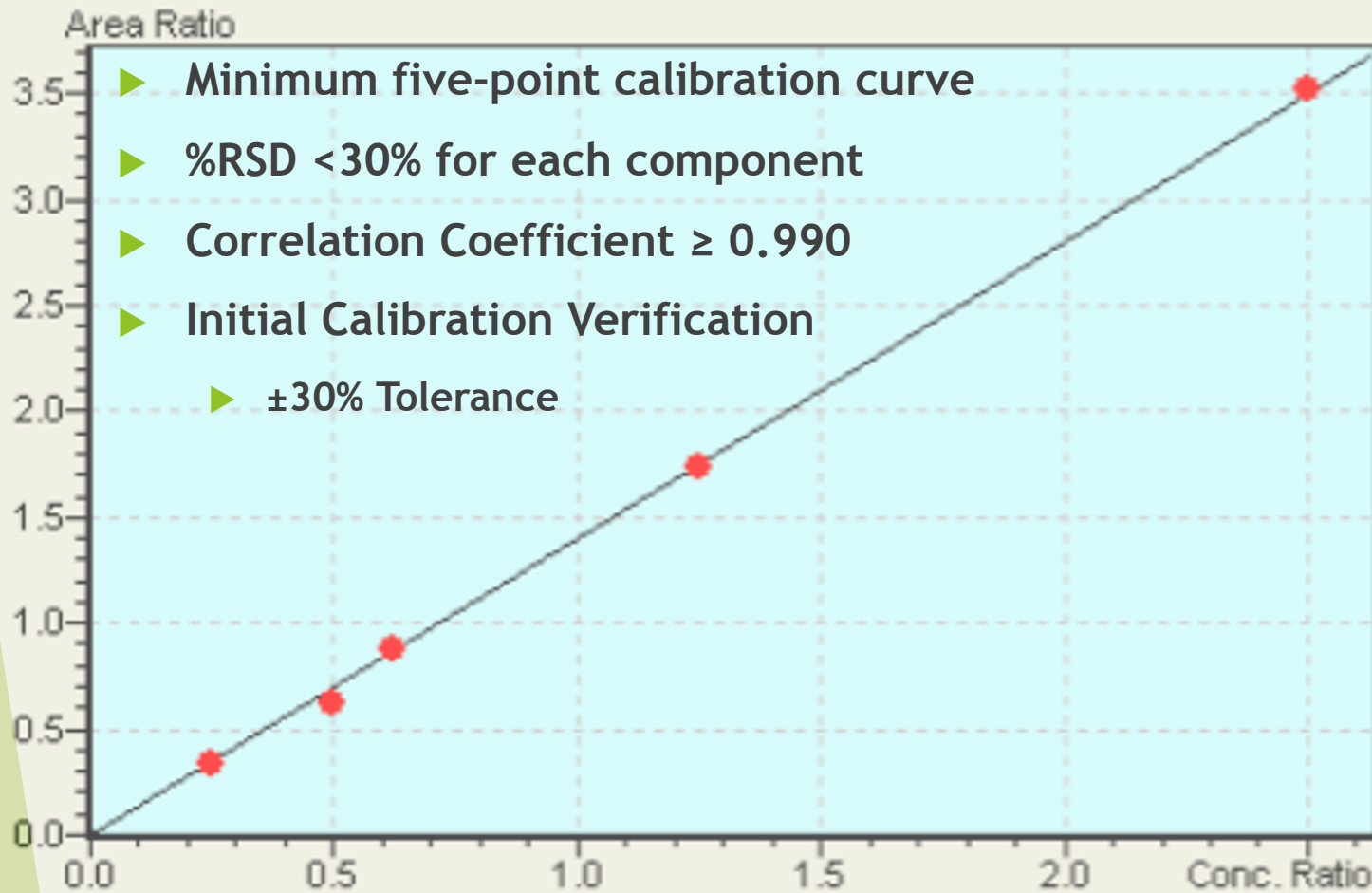


Atomic Emission (GC-AED)



Inductively Coupled Plasma Mass Spectrometry (GC-ICPMS)

ASTM D8230-19: Calibration Requirements



- ▶ Minimum five-point calibration curve
- ▶ %RSD < 30% for each component
- ▶ Correlation Coefficient ≥ 0.990
- ▶ Initial Calibration Verification
 - ▶ $\pm 30\%$ Tolerance

$Y = 1.399148X + 0.0$
 $R^2 = 0.9992863$
 $R = 0.9996431$

Internal Standard
Curve: Linear
Origin: Force Through
Weighting Method: None

Mean RF : 1.356177
RF SD : 0.0749259
RF %RSD : 5.524784

ASTM D8230-19: QA/QC Requirements

- ▶ Calibration check
 - ▶ Minimum once per day, or every 10 samples
 - ▶ $\pm 30\%$ Tolerance
- ▶ Laboratory Control Standard
 - ▶ Matrix Spike during sample sequence
 - ▶ $\pm 30\%$ Tolerance
- ▶ Replicate Precision
 - ▶ One duplicate analysis per sample set or ten samples
 - ▶ $\pm 25\%$ Tolerance
- ▶ Desorption Efficiency Study for sorbent tubes
 - ▶ Minimum annually
 - ▶ Average recovery $> 75\%$ for each analyte



ASTM D8230-19: What's not Included

- ▶ Methanol impingers
 - ▶ Sought authors during development phase
 - ▶ Fallen out of favor among users represented in WK52796
- ▶ Sorbent Tube Thermal Desorption
 - ▶ No users of this method in workgroup
 - ▶ Single use vs. solvent extract multiple use
- ▶ GC-VUV
 - ▶ Method not fully developed
- ▶ These techniques could be included in future revisions

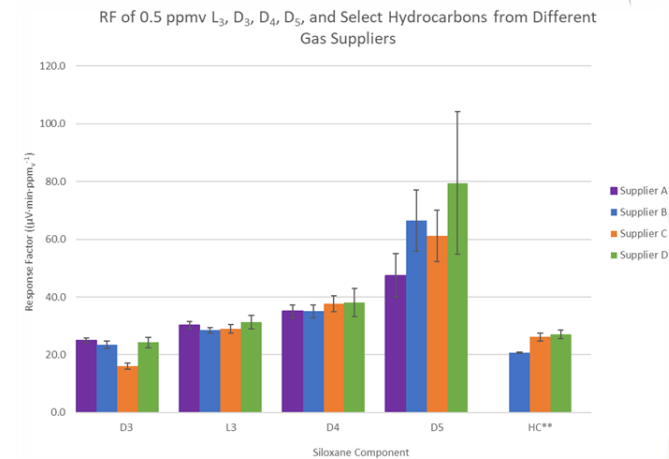


GTI: Related Work in Progress



▶ OTD Project 7.16.g.2

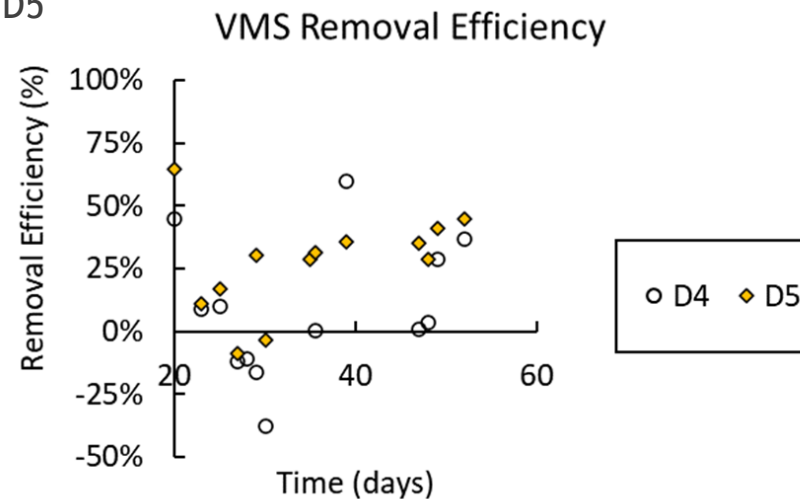
- ▶ Evaluation of identical siloxane gas standards from known suppliers
 - ▶ Results will determine supplier(s) of mixtures used for the ASTM D8230-19 InterLaboratory Study (ILS) to determine the method precision and bias
 - ▶ 3 blind siloxane gas mixtures supplied to labs for analysis
 - ▶ A minimum of 6 laboratories participating
 - ▶ Still recruiting labs, contact if interested!
- ▶ Evaluation of on-line siloxane analyzer at RNG landfill site
 - ▶ Three-month evaluation period testing real-world RNG
 - ▶ Periodic grab sample collection to compare online data to ASTM D8230-19 analysis



GTI: Related Work in Progress



- ▶ SMP Project 22596 - Development of new siloxane removal technology
 - ▶ In conjunction with Duke University
 - ▶ Have developed a biotrickling filter capable of converting CO_2 to CH_4 in the presence of H_2 utilizing hydrolysis
 - ▶ Objective: Further develop biotrickling filter to simultaneously scrub H_2S and siloxanes in addition to converting CO_2 to CH_4
 - ▶ Initial testing shows reduction of D4 & D5 siloxanes
 - ▶ A matter of finding the right balance between competing pathways and nutrient requirements within the biotrickling filter media



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