Field Validation of an On-Line FTIR Analyzer for Measuring Total Siloxane Content in Landfill Gas

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Technology for Productivity

Why Monitor Siloxanes in Biogas?

- Assess Biogas Fuel Quality
  - Quantify Methane and CO_2 content
  - Verify composition before gas enters pipeline
  - Verify impurity levels

- Siloxane Impurities
  - High temperature: SiO2 powders form
  - Turbines - mechanical wear and tear
  - Boilers - particulate build up – increase in maintenance frequency
  - SCR Catalysts – plugged in minutes
  - Micro-turbines can be destroyed
- 2009 Engine MFG Siloxanes Limits in mg/m^3
  - Caterpillar 28
  - Jenbacher 10
  - Waukesha 25
  - Deutz 5
  - Solar Turbines 0.1
  - IR Microturbines 0.06
  - Capstone Microturbines 0.03

Traditional Landfill Gas Siloxane Sampling and Analysis

- Process
  - Landfill gas sample collected at site
  - Sample sent to off site analytical lab
  - Analysis results generally take 1 week turn around time

- Traditional Sampling Methods
  - Extraction / Concentrators
    - **Thermal Desorption tubes (Tenex)**
    - Impingers (methanol)
    - **JetCare** (oil-based extraction)
    - Extra processing needed to release or determine Siloxane content
  - Direct Sampling Methods
    - **Tedlar bags**
    - Suma Canisters
      - Canisters must be coated with glass

Issues with Traditional Sampling Methods

- Difficultly in sending gas samples across borders
  - Interstate as well as national border issues
- Not representative
  - One shot analysis over 2 – 30 minutes
- Sample prep or conditioning required
  - Remove H_2O
  - Concentrate sample
  - Recover / extract from media - Some Siloxanes unrecoverable
- Inconsistencies in reported results for duplicates
  - Sample handling issues
  - Conversion of TMS and Siloxanes during transportation, due to media or H_2O content

FTIR as the Alternative Siloxane Sampling & Analysis Tool

- On Site continuous sampling and analysis
  - Pre- and Post-Scrubber analysis with same instrument
- No sample gas conditioning required
  - Sample gas pressure used to flow gas into FTIR
  - H_2O removal not required
  - Rapid Analysis
    - 20 seconds to 1 minute
- FTIR detects multiple species at same instance
  - Siloxanes have strong FTIR signal – ppb detection
  - CH_4, CO_2, H_2O – from ppb to percent level
  - Analyze for other components as well
    - NH_3, CO, COS, Hydrocarbons, etc.

MKS Patented Total Siloxane Method

- Does not provide speciated Siloxane numbers
  - Not needed – only useful for filter development
- Provides one number for all of the main straight chain (L2-L5) and cyclic (D3 – D6) siloxanes
- Reports Trimethylsilanol (TMS) as well as Total Si at current CH_4 content
  - **Total Siloxanes** as **mg/m³** and **Si (mg/m³)**
  - **Total TMS** as **mg/m³** and **Si (mg/m³)**
  - **Total TMS and Siloxanes** as **Si (mg/m³)**
  - Scale reported values to the Laboratory value
- Calibrations based upon Permeation Devices
  - Permeation device mechanism NIST Traceable

FTIR Landfill Gas Siloxane Analysis

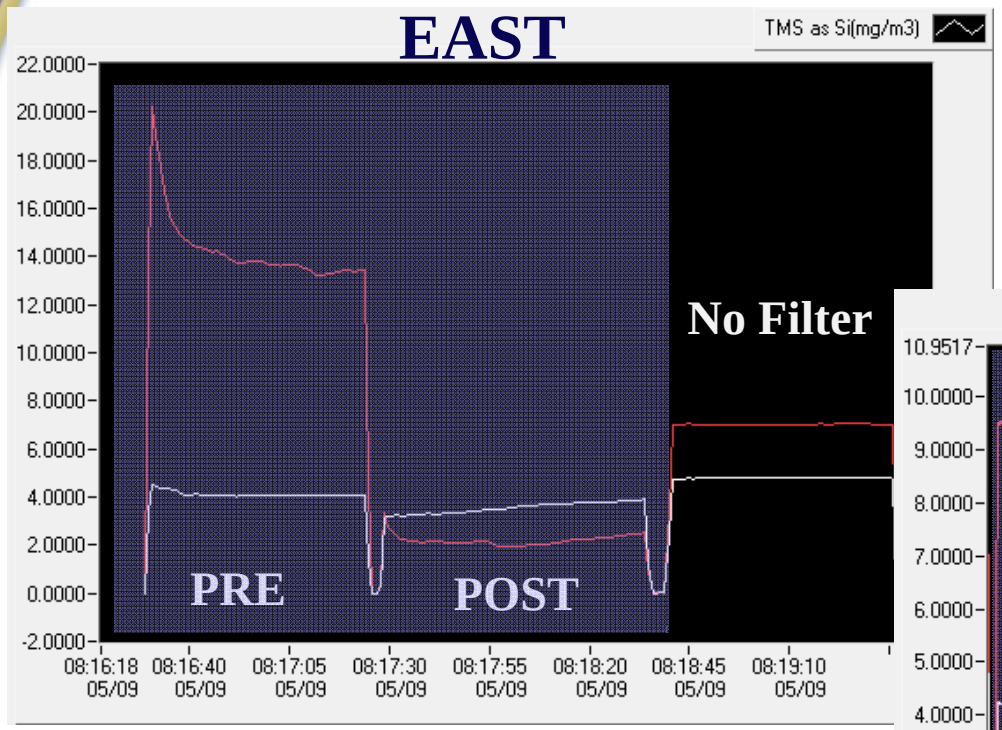
- MKS AIRGARD® FTIR
  - Transported to Landfill port via hand cart (75 lbs)
  - Setup < 15 minutes
  - Continuous analysis - 60 sec scan time
  - Total Siloxane method used
    - Conservative Detection Limit 0.2 mg/m^3
- Landfill Sites – 9 Total
  - Three sites had Siloxane scrubber systems
    - Different filter media at each site
  - 7 sites collected Tenex adsorption tubes
  - 1 site collected Tedlar Bag

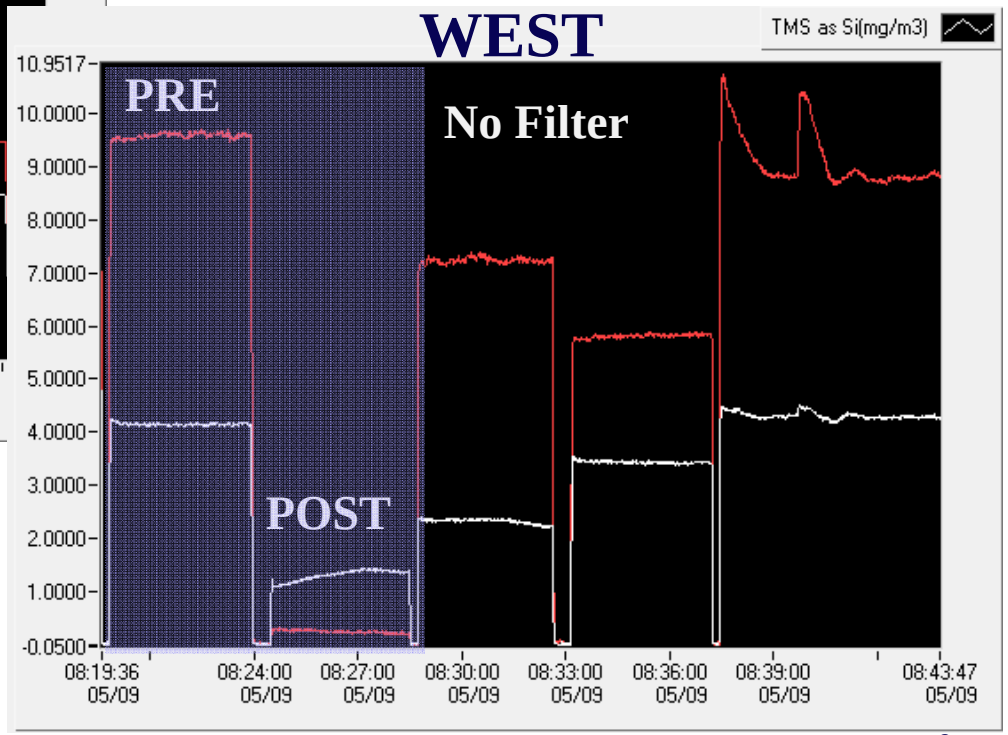
Total Siloxane Landfill Gas Analysis Validation Process

- Goal
  - Use lab analysis on gas sample to validate FTIR method in the field
- Field Collection Process
  - Collect FTIR Landfill gas data
    - Gas Spectra for Raw and Processed Landfill gas
    - Run continuously at 1 minute rate
  - Collect Landfill Gas Samples for Laboratory Analysis
    - Collect duplicate samples
    - Tenex spaced 30 minutes apart due to gas collection time
    - Tedlar bag collections immediately after Tenex collection
  - Send gas samples to preselected labs
- Use Lab results to validate the FTIR field Data
  - Use FTIR Total Siloxane method
  - Scale the Total Siloxane value to the Lab reported results

FTIR Total Siloxane Analysis

East (2) and West (4) Sites





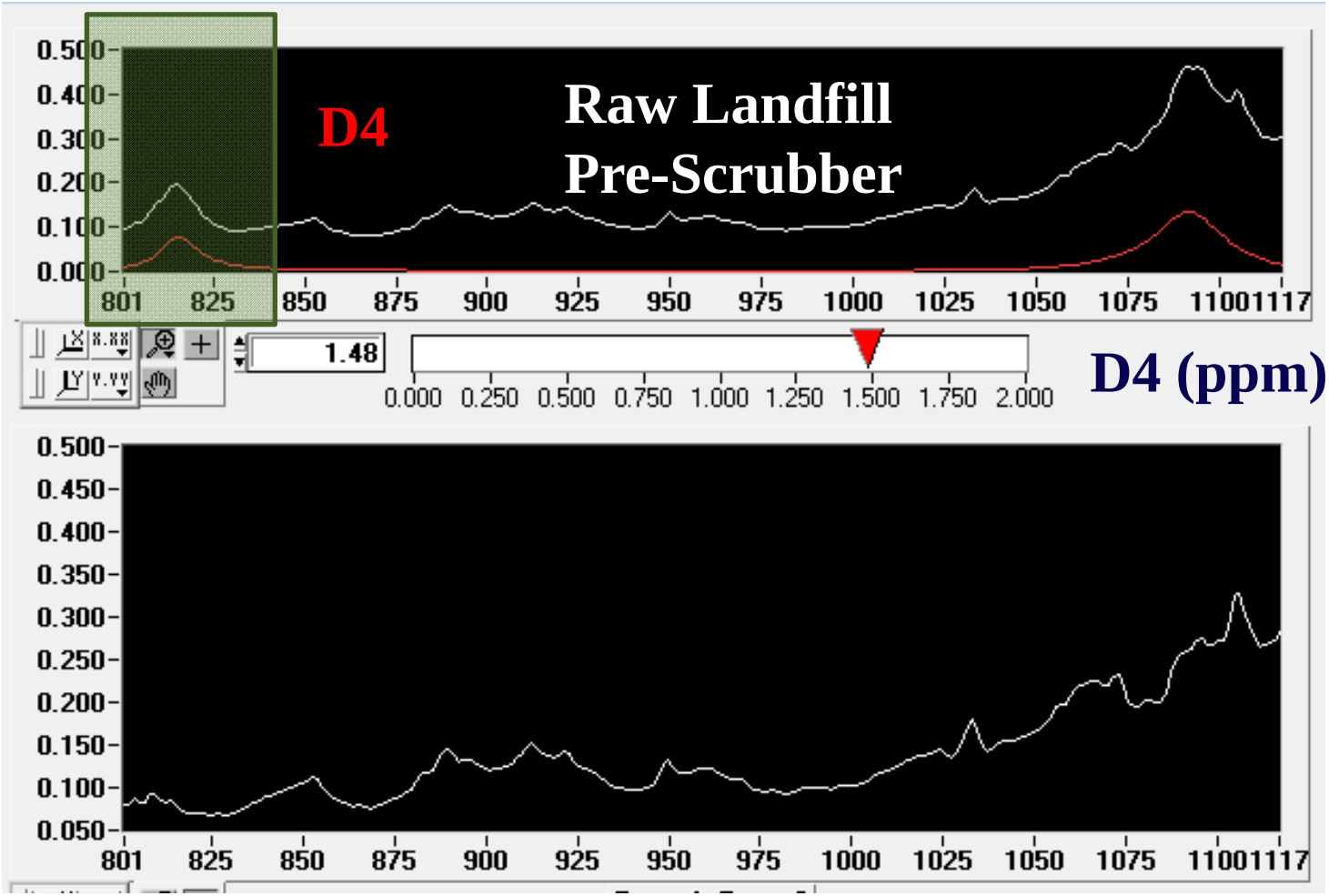
RED **Total Siloxane** (Si mg/m^3)
WHITE Total TMS (Si mg/m^3)

Example of Same Laboratory Different Landfill Discrepancies

Site	Tenex TMS (Si mg/m^3)	FTIR TMS (Si mg/m^3)	Tenex Total Siloxane (Si mg/m^3)	FTIR Total Siloxane (Si mg/m^3)
East #1 Pre-scrubber	3.3	3.35	12.7	14.7
East #1 Post-scrubber	0.35	2.8	4.7	4.4
East #2 No scrubber	3.9	4.1	8.1	9.4
West #1 Pre-scrubber	7.9	2.7	3.1	9.4
West #1 Post-scrubber	0.11	0.8	2.2	<0.2

Component	Tenex Inlet1	FTIR	Tenex Outlet1	FTIR
TMS	6.552	2.330	0.103	0.63
L2	0.619	0.600	0.019	0.001
D4	0.346	1.670	0.407	0.018

PPM not
Si (mg/m^3)



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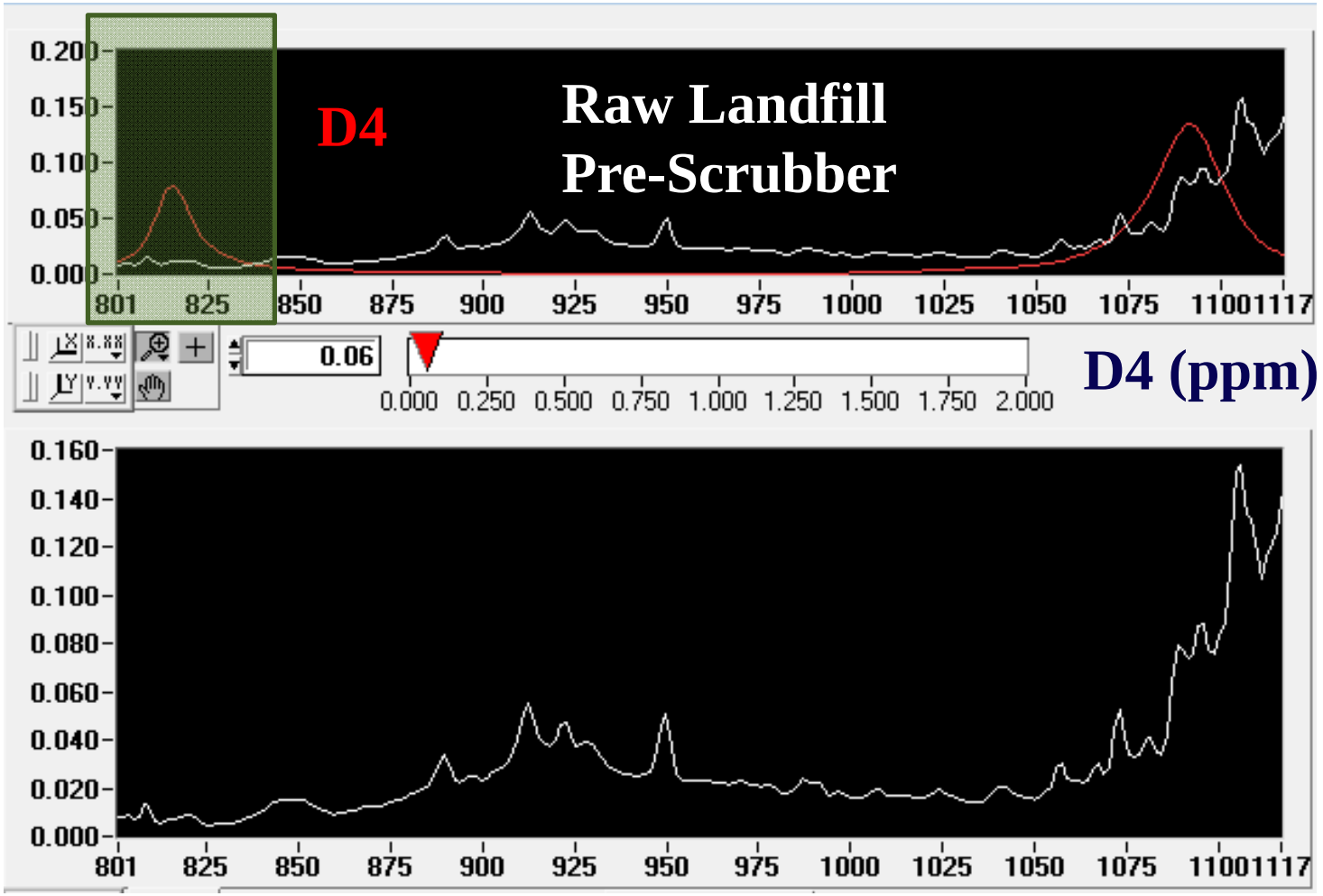


Example of Single Landfill Multiple Laboratory Discrepancies

	Scrubber Inlet WET / RAW (Si mg/m3)				
	Tedlar AnSol	**Tedlar OSB**	**TENAX CAS**	**FTIR**	**JetCare***
(1) Siloxane	11.292	12.480	13.143	17.661	
(1) Siloxane+TMS	14.812	18.536	18.943	24.317	110.080
(2) Siloxane		3.407	16.304	17.867	
(2) Siloxane+TMS		6.797	22.704	24.725	
	Scrubber Inlet DRY (Post Chiller) (Si mg/m3)				
	Tedlar AnSol	**Tedlar OSB**	**TENAX CAS**	**FTIR**	**JetCare**
(1) Siloxane	10.508	10.606	9.981	17.546	
(1) Siloxane+TMS	13.608	14.950	15.481	24.382	81.801
(2) Siloxane		9.432	15.198	17.556	
(2) Siloxane+TMS		14.795	22.798	24.146	
	Scrubber Outlet (Si mg/m3)				
	Tedlar AnSol	**Tedlar OSB**	**TENAX CAS**	**FTIR**	**JetCare**
(1) Siloxane	0.838	0.647	1.558	1.896	
(1) Siloxane+TMS	0.838	1.131	1.650	2.715	7.174
(2) Siloxane		0.563	1.681	2.169	
(2) Siloxane+TMS		0.971	1.791	2.982	

* Reports Total Si which includes particulates as well as volatiles

Method Validation Issues

- Which Golden Standard do you use for comparison or scaling?

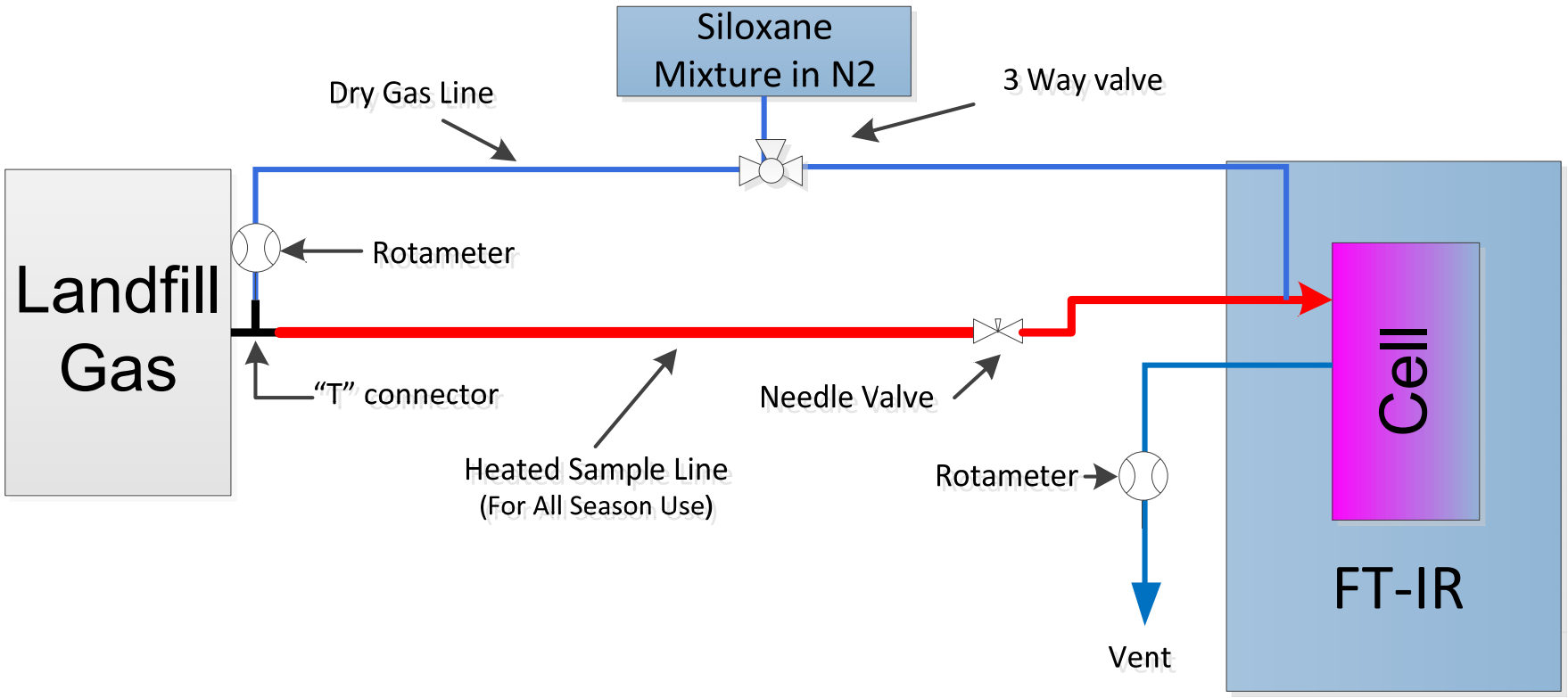
	Scrubber Outlet (Si mg/m3)			
	Tedlar AnSol	Tedlar OSB	TENAX CAS	FTIR
(1) Siloxane	0.838	0.647	1.558	1.896
(1) Siloxane+TMS	0.838	1.131	1.650	2.715
(2) Siloxane		0.563	1.681	2.169
(2) Siloxane+TMS		0.971	1.791	2.982

- Which Laboratory is correct?
  - Duplicate samples are inconsistent
  - One lab did not detect TMS all others did
- What sampling method is correct?

FTIR Field Validation Process Using Analyte Spiking

- Analyze the FTIR Response to the Spike Gas
  - Run the Landfill gas sample through the FTIR
  - Dilute 10% of landfill gas with “known” Siloxane mix (Spike)
- Validate the FTIR Response
  - Use the CO_2 response to determine the dilution amount
  - Calculate how much Siloxane should reach the FTIR in the diluted stream
  - Calculations
    - Determine Native Siloxane – run Landfill gas only
    - Determine Siloxane content of the undiluted Siloxane Gas Mixture
    - Determine Siloxane content during the 10% Spike
    - Calculate the % Recovery (Actual Spike / Expected Spike)
    - If within ± 30% Expected Value then this is “validated”

Analyte Spike Experimental Setup



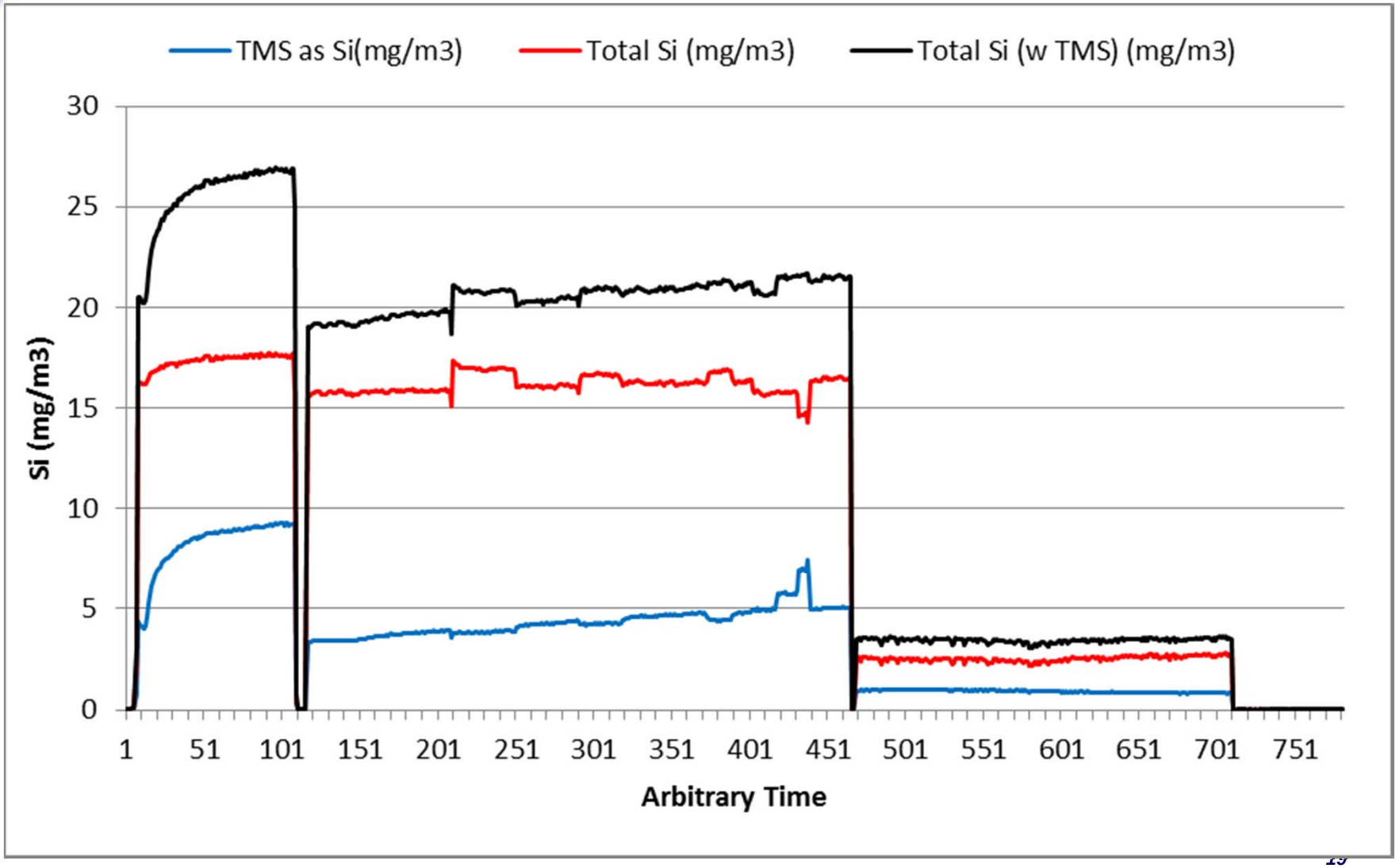
On Site Field Validation Study

- GC/FID for External Validation
  - Analytical trailer equipped with GC/FID transported to site
  - 12 min / full scan
  - Used to validate Siloxane Mixture and Spikes
- FTIR
  - MKS AIRGARD transported to site
  - 1 min / scan

Field GC / FID Issues

- GC/FID equipment available for only one day
- Requires daily field calibration
  - Calibration standards necessary for on-site analysis
- Permeation tubes used for Siloxane calibrations
  - >2 hours run time for stable permeation reading
  - Permeation Tubes bundled to shorten wait time
    - Bundled tubes produced incorrect concentrations
      - Results were reproduced later in the lab
    - Conversion of siloxanes in the permeation oven
    - Incomplete permeation of other siloxanes
  - Initial concentration of TMS in Tedlar bag unknown
- Unable to verify GC Peaks in the field
  - Concentrations measured by GC are unknown
  - Direct GC to FTIR comparison unable to be performed
  - Need better Field transportable Siloxane and TMS standards

Landfill Siloxane and TMS Spike Tests



Other Issues Related to Siloxane Field Validation

- Sampling Methods
  - Shipping samples – Customs, DOT Hazard forms
  - Conversion of L2, D3, D4 and TMS to other compounds
- Field Calibration Methods
  - Permeation Device
    - Only one tube in oven at any one time
    - Time to equilibrium extremely long
    - Higher concentrations not accurate
  - Syringe Pump
    - Hard to vaporize
    - Low concentrations only
    - Mixtures can be made using Hexane solution
  - Cylinders
    - Siloxanes stick to the walls
    - Cylinders not readily available
    - Not certified
    - Not in high concentrations

Field Validation Method

Proposed Modifications (Brown)

- **Use Cylinder Gas Mixtures**
  - **(A) Purchase from Gas Supplier**
    - **TMS needs its own cylinder**
    - **Siloxanes blended in a cylinder**
  - **(B) Or create own using siloxane blends using diffusion method**
    - **Yet to be tested**
    - **Must be in Summa Canisters**
  - **(C) Use Syringe Pump**
    - **Mix with Hexane to vaporize**
- **Analyze Cylinder gases response on FTIR prior to shipping**
  - **Send equipment and cylinders to site**
- Analyze the FTIR Response to the Spike Gas
  - **Run Cylinder gases response on FTIR at Site prior to Spike Test**
  - Run the Landfill gas sample through the FTIR
  - Dilute 10% of landfill gas with “known” Siloxane mix (Spike)
- Validate the FTIR Response
  - **Use MFCs for Landfill gas and Spike gas if possible**
    - **Or at least use MFC for Spike gas and CO_2 for dilution amount**
  - Calculate how much Siloxane should reach the FTIR in the diluted stream
  - Calculations
    - Determine Native Siloxane – run Landfill gas only
    - Determine Siloxane content of the undiluted Siloxane Gas Mixture
    - Determine Siloxane content during the 10% Spike
    - Calculate the % Recovery (Actual Spike / Expected Spike)
    - If within ± 30% Expected Value then this is “validated”

Proposed ASTM Field Validation Method

- FTIR, Gas cylinders and field equipment ready
- Currently looking for site near Raleigh, NC
  - Prefer site with Siloxane Removal system and existing GC (or other analyzer) for Siloxanes comparison
- Multi-Analyzer Round Robin
  - Round Robin tests at Los Angeles County Sanitation District (LACSD)
  - Analyze samples in the field as well as in the lab at same time as GC-ICP, GC-MS
  - Send field collected samples to various labs for analysis:
    - Tenex
    - Methanol Impingers
    - Tedlar bag
    - Summa Canisters
- Create ASTM Test Methods
  - Lab GC-XX – Sally Mathison LACSD
  - FTIR Field Method – Barbara Marshik MKS Instruments

Summary

- MKS AIRGARD® FTIR Technology
  - Clearly capable of analyzing siloxanes and TMS to very low concentrations
  - At-line analysis in high level CH_4, CO_2 and H_2O
  - Fixed installations or transportable to site
- Total Siloxane and Total Silicon Method
  - Works well in raw or scrubbed biogas applications
  - TMS and Siloxane continuous monitoring at <0.2mg/m^3
- FTIR Field Validation
  - Laboratory analysis varies so too much to determine which is correct
  - Better FTIR MDLs can be provided once field validation is completed