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

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Presented at the 2014 LMOP Conference

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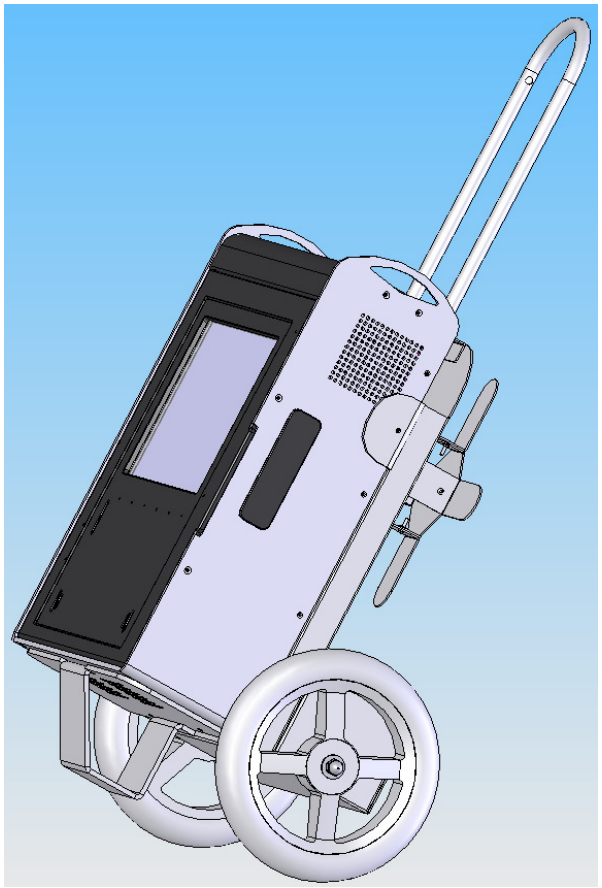
Technology for Productivity

MKS Instruments
AIRGARD® FTIR

- MKS AIRGARD® FTIR Technology
  - 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



Issues with Current Sampling/Analysis Methods

Sampling Methods

- Process
  - Landfill gas sample collected at site
  - Sample sent to off site analytical lab
  - Analysis results generally take 1 week turn around time
- Extraction / Concentrators
  - **Thermal Desorption tubes** (Tenax)
  - **JetCare** (oil-based extraction)
  - Impingers (methanol)
  - Extra processing needed to release or determine Siloxane content
- Direct Sampling Methods
  - **Tedlar bags**
  - Suma Canisters
    - Canisters must be coated with glass

Laboratory Analysis

- Difficultly in sending gas samples
  - Interstate as well as national border issues
- Not representative
  - One shot analysis over 2 – 30 minutes
- Sample prep or conditioning required
  - Remove H2O
  - Concentrate sample
  - Recover / extract from media - Some Siloxanes unrecoverable
- Long analysis time
  - 3 days up to a week TAT
- Inconsistent Results
  - Duplicates (if taken) can be completely different
  - No gas standards available
  - Multiple laboratories do not always agree
  - Sample handling issues
  - Conversion of TMS and Siloxanes during transportation, due to media or H2O or other gases in biogas sample

Example of Single Landfill Multiple Laboratory Discrepancies

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

* Calc converting from Si on a CH4 basis to Si = Si(CH4 Basis)*CH4 (in Percent) / 100

Field Validation Method

Analyte Spike Recovery Method

- Gas Mixtures
  - (A) Purchase cylinders from Gas Supplier
    - TMS needs its own cylinder
    - Siloxanes blended in a cylinder
    - Analyze Cylinder gases response on FTIR prior to shipping
    - Send equipment and cylinders to site
  - (B) Use Syringe Pump
    - Mix with Hexane to vaporize – issues with Solvent
- 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 – Native Siloxane content
  - 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 CO2 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”