Real-Time Siloxane Measurements at Landfill and Digester Sites using FTIR

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Biogas

- Alternative Source for Compressed Natural Gas
  - Renewable and local source of energy
    - Landfills, Digesters, Farm waste
  - Excess Biogas sent to CNG pipeline

- What are the Concerns?
  - Liquid Natural Gas
    - Higher BTUs – US appliances not able to use
    - Very clean fuel source
  - Compressed Natural Gas from Asia
    - Higher BTUs – US appliances not able to use
    - Pipeline owners want BTU range restricted
  - Biogas
    - Impurities – Siloxanes and Chlorinated HCs
    - CH4 ~40 - 60%, rest is CO2

- How and Who will monitor these alternative sources?
What to Monitor?

- Assess Fuel quality before gas enters pipeline
  - Quantify Methane and CO2 content
  - Determine BTU content

- Determine Impurity Levels
  - Siloxane and Chlorinated impurities
  - Prevent impurities from entering natural gas pipeline
    - Minimizes system maintenance cost
  - At high temp operation SiO2 and SiO3 powders form
    - Turbines: mechanical wear and tear
    - Boilers: particulate build up
Current Siloxane Analysis

- **Method:** GC – ICP – MS
  - **Sampling Methods**
    - Solvent Extraction
    - Thermal Desorption tubes
    - Tedlar bags – components stick
    - Suma Canisters – must be coated with glass
    - Impingers
  - **Issues**
    - Not on line sampling
    - Sample must be conditioned first (remove H2O)
    - Sample must be concentrated
    - Some Siloxanes unrecoverable
    - Sampling time long
      - 15 to 30 minutes after sample collection
Why FTIR?

● **Sampling Conditions**
  - On line sampling can be done
    ● Gas pulled straight from filter to FTIR
  - No sample conditioning needed
  - Continuous Emission Monitoring (CEM) capability

● **FTIR Analysis**
  - FTIR detects multiple species at same instance
    ● CH4, CO2, H2O, CO, Hydrocarbons, Siloxanes, etc.
    ● Percent down to ppb or lower concentrations
  - Siloxanes have strong FTIR signal – single digit ppb
    ● L2 – L4 straight chain siloxanes
    ● D3 – D6 cyclic siloxanes
  - Rapid Scanning and analysis
    ● 20 seconds to 1 minute
Infrared (IR) Spectroscopy

- Based on IR light absorption
  - Energy (IR radiation) heats molecule - vibrations and rotations
  - The pattern and intensity of the spectrum provides all the information about gas (type and concentration)
Siloxanes and Hydrocarbons

- D3
- D4
- D5
- Ethane
- Butane
- Propane
- L4
- L3
- L2
Current Studies

● Cylinder Dilution Study
  – Test Speciation versus Surrogate Methods
  – Gas Mix
    ● 540ppb of L2, L3, L4, D3, D4, D5 Siloxanes in CH₄
    ● 100% CH₄ used for blending
  – Dilution Factor not specified
  – MKS MG2030 FTIR
    ● 5.11m gas cell
    ● 40 C, ~ 20 sec data averaged to 100 sec

● Digester Dilution Study
  – Test Speciation versus multiple Surrogate Methods
  – Gas direct from digester then diluted with CH₄
    ● Mainly D4 and D5 (75:25)
    ● ~60% CH₄, ~40% CO₂ plus some Ethane and Propane
  – MKS AIRGARD
    ● 10.18m gas cell
    ● 40 C, ~20 sec data averaged to 100 sec
Cylinder Study
Speciated vs Surrogate

Cylinder Blend Tests

Speciated
Surrogate #2
Surrogate #2 (x1.25)

3.11 ppm-v

Cylinder Dilution Expanded View
Dilution of Total Siloxane (3.24 ppm-v) in 100% CH₄
Raw Digester Gas

- CH4
- C2H6
- C3H8
- CO2
- D4
Digester Dilution Study – Speciated

Speciation Method Comparison

- Dilution Calc
- Speciated, HC#1
- Speciated, HC#2
- Surrogate #1, HC#1
- Surrogate #1, HC#2

Total Siloxanes (ppm-v)
Digester Dilution Study – Surrogates

Surrogate Method Comparison

- Total Siloxanes (ppm-v)

- Dilution Calc
- Surrogate #1
- Surrogate #2
FTIR – Current Studies Summary

- **Siloxane Speciation Method**
  - L2 – L4 straight chain siloxanes
  - D3 – D6 cyclic siloxanes
  - DLs ~ 300 - 500 ppb level
  - Suffers from high cross sensitivity to hydrocarbons

- **Siloxane Surrogate Method**
  - Mixture of cyclic and straight chain siloxanes
  - DLs ~ <50 ppb level total Siloxanes
  - Very low variance in the signal response
  - Low sensitivity to hydrocarbons
  - Tracks dilution study well but accuracy off
  - May require a correction factor – TBD
Next Steps - <50 ppb level Total Siloxane Analyzer

- Collect at line FTIR Landfill and Digester data
- Use the Filtered gas streams – not raw
- Collect grab samples for cross validation points
- Perform careful spike dilution tests
  - Use filtered LFG or DG gas streams in the field
  - Use MFCs, Certified Cylinders with internal spike gas for blending