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

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Technology for Productivity

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

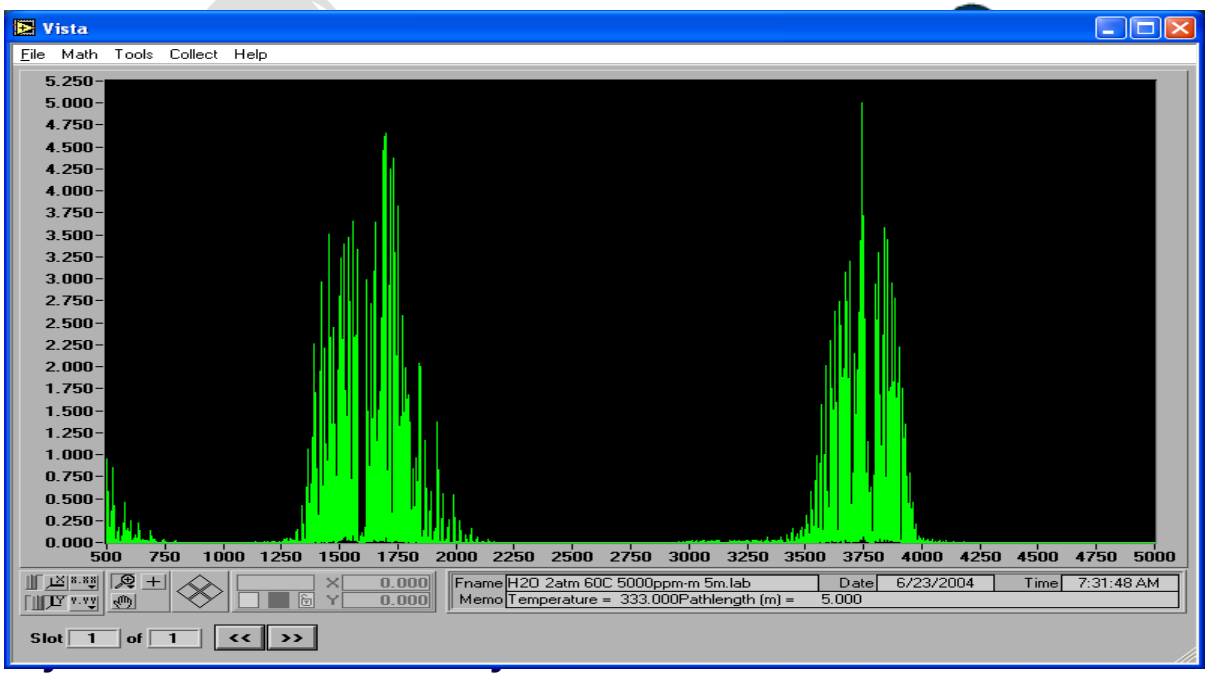
- Method: GC – ICP – MS
  - Sampling Methods
    - Solvent Extraction
    - Thermal Desorption tubes
    - Tedlar bags – components stick
    - Suma Canisters – must be coated with glass
    - Impingers
  - Issues
    - Not on line sampling
    - Sample must be conditioned first (remove H2O)
    - Sample 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)



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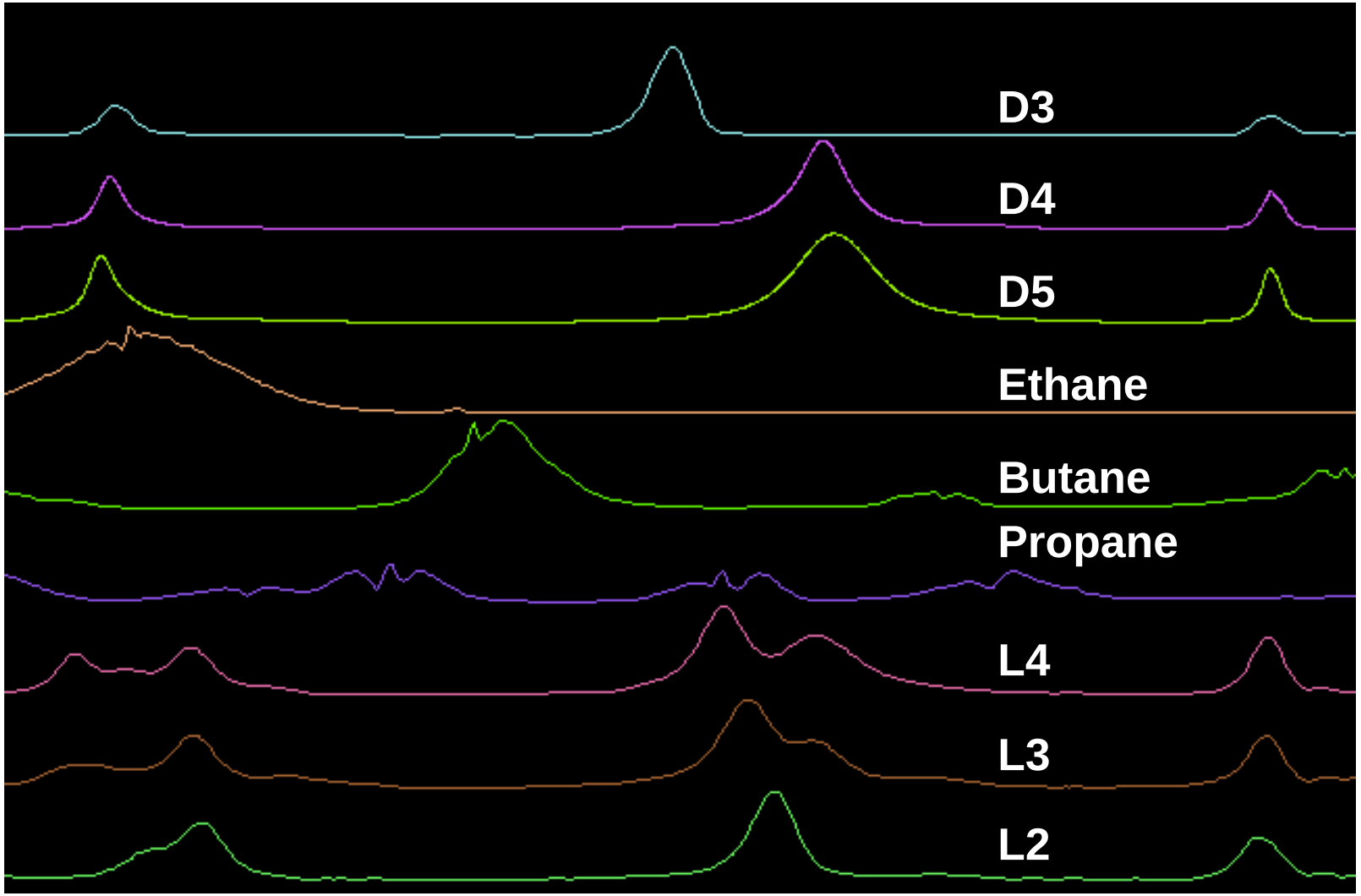
Siloxanes and Hydrocarbons

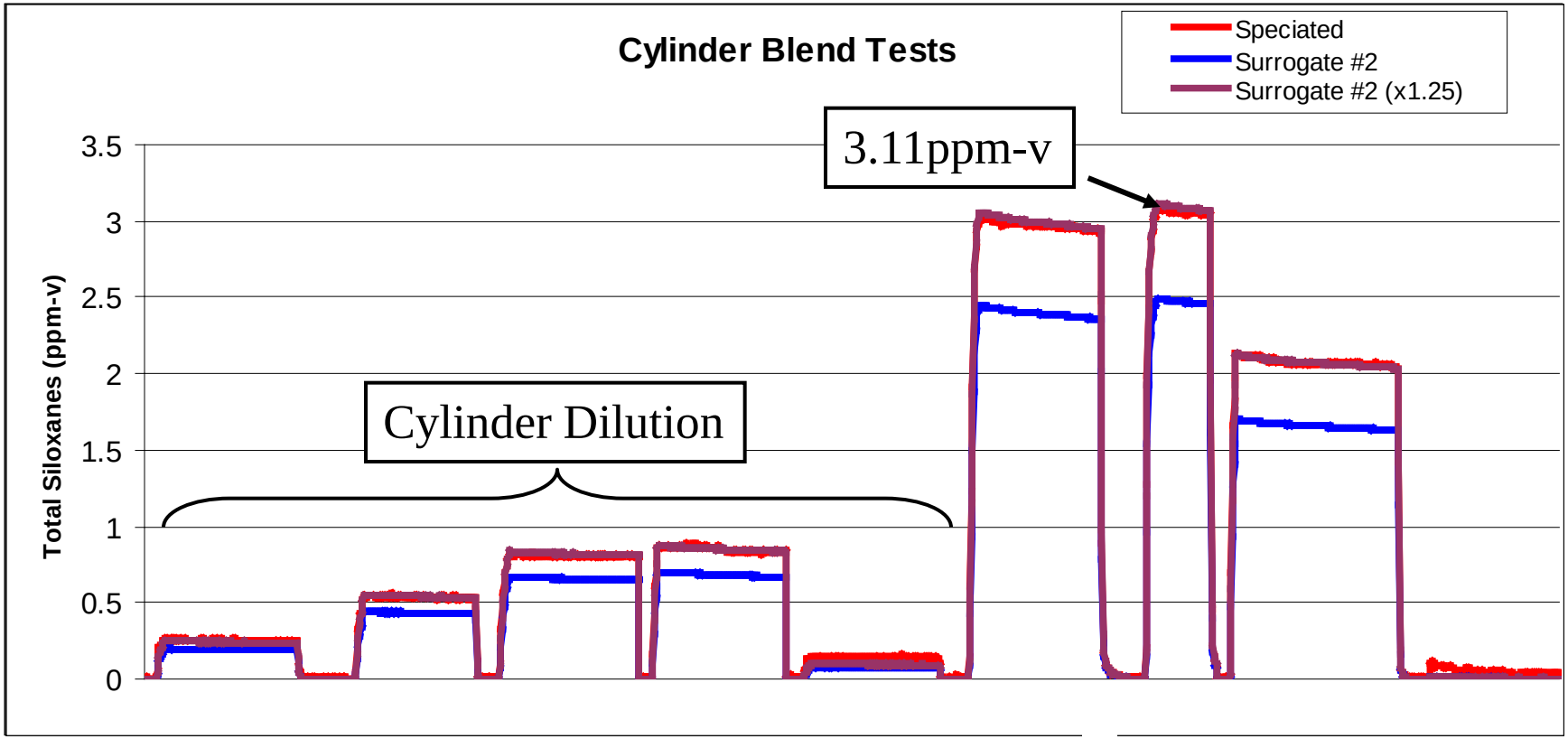


Current Studies

- Cylinder Dilution Study
  - Test Speciation versus Surrogate Methods
  - Gas Mix
    - 540ppb of L2, L3, L4, D3, D4, D5 Siloxanes in CH_4
    - 100% CH_4 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 CH_4
    - Mainly D4 and D5 (75:25)
    - ~60% CH_4, ~40% CO2 plus some Ethane and Propane
  - MKS AIRGARD
    - 10.18m gas cell
    - 40 C, ~20 sec data averaged to 100 sec

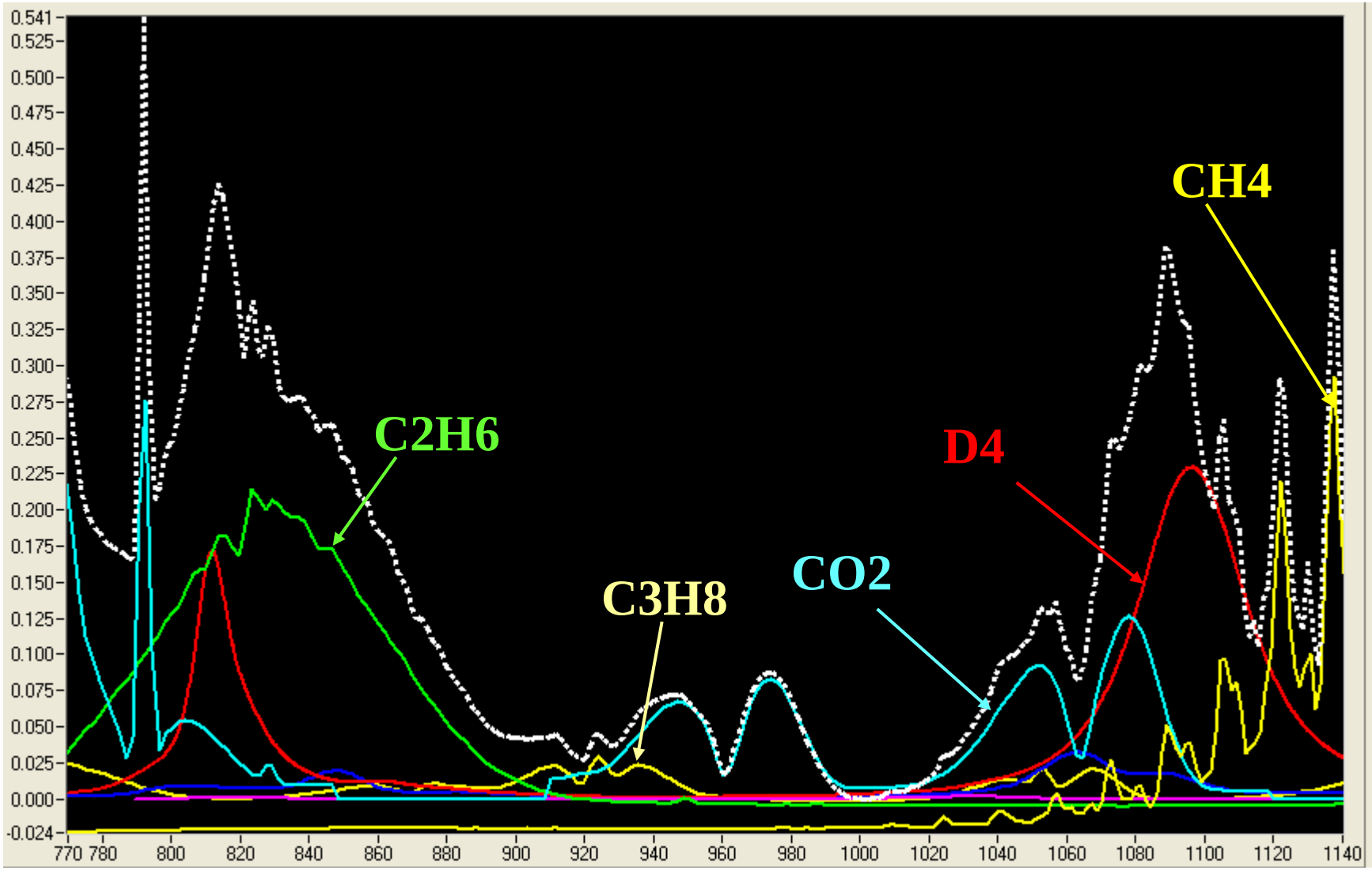
Cylinder Study

Speciated vs Surrogate

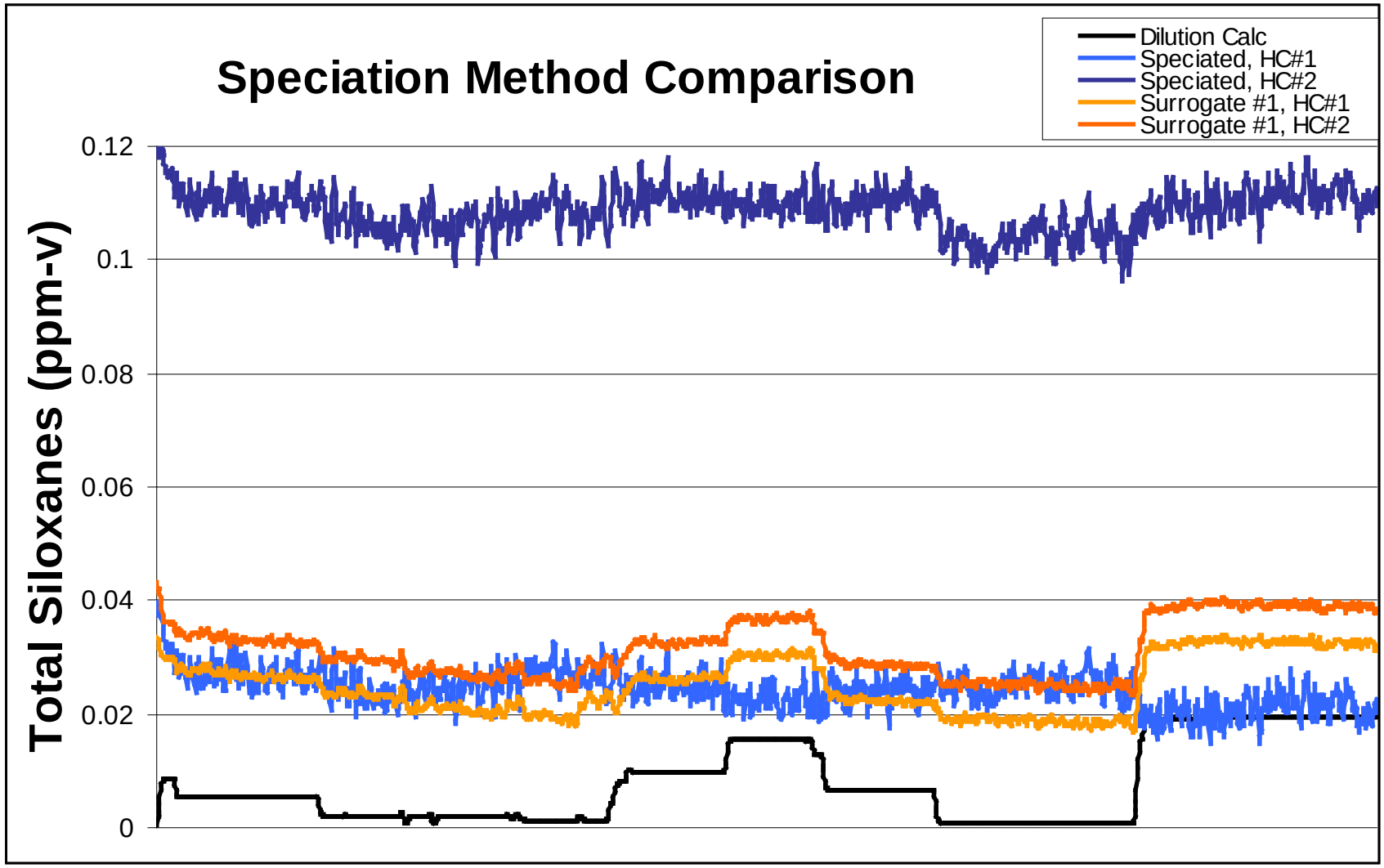


Cylinder Dilution Expanded View
Dilution of Total Siloxane (3.24 ppm-v) in 100% CH_4

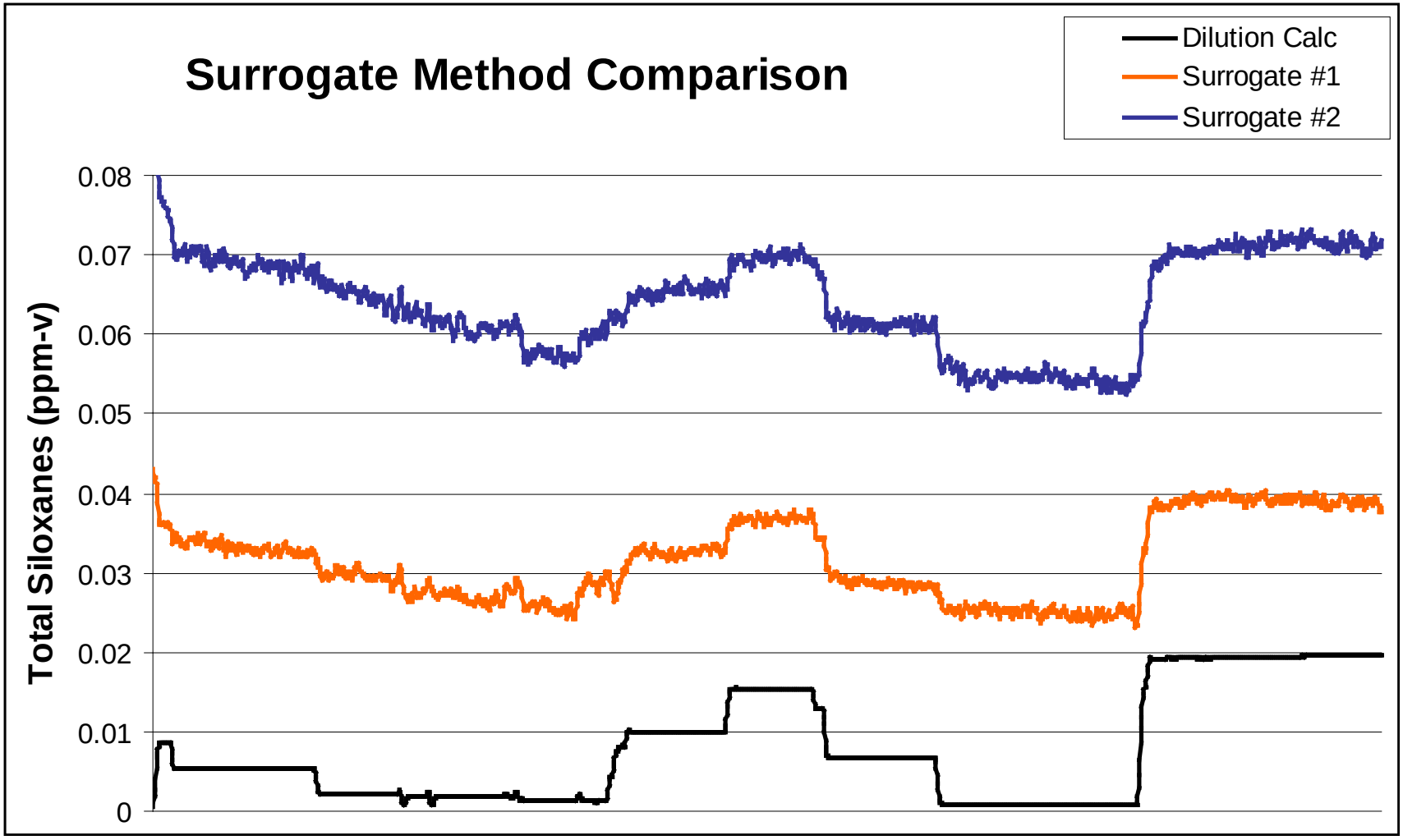
Raw Digester Gas



Digester Dilution Study – Speciated



Digester Dilution Study – Surrogates



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