# GMRC 2011

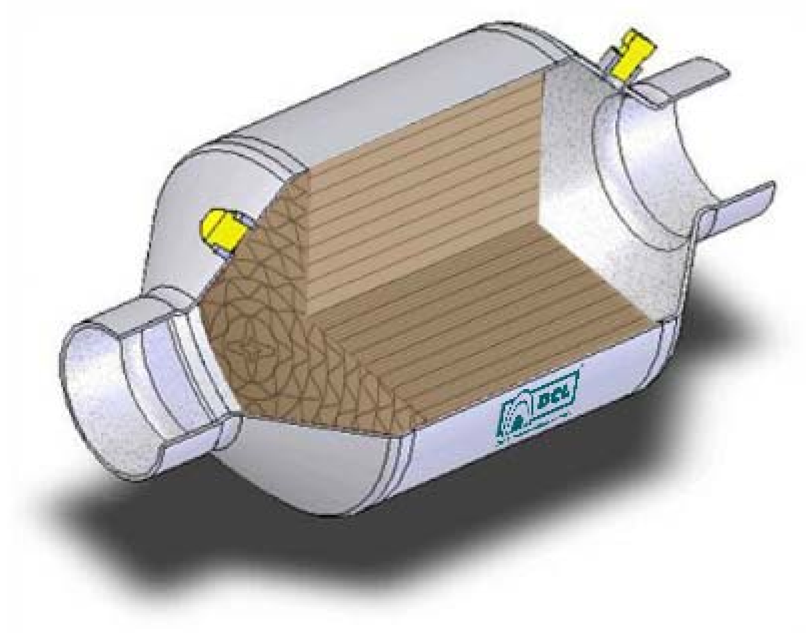
# Understanding FTIR formaldehyde measurement and its influence on the RICE NESHAP rule

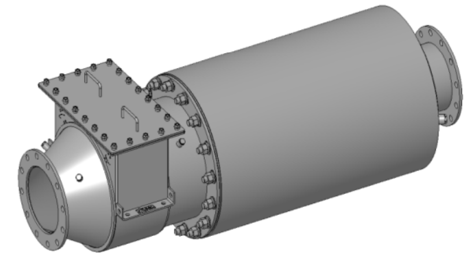

Authors: Shazam Williams, Joe Aleixo, Robin Hu, Yuki Leung

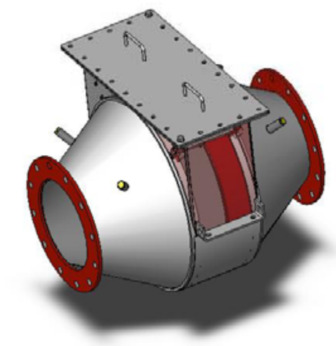
Company: DCL International Inc.

# DCL Overview

Manufacturer of catalytic emission controls for industrial engines, off-road and stationary







# Outline

- Background
- Experimental
- Results and Discussion
- Implication of Results on Field Testing
- Conclusion

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# Background

- In 2010, the EPA finalized a national regulation for reducing emissions from stationary compression ignition (CI) and spark ignition (SI) engines.
  - Reciprocating Internal Combustion Engines National Emission Standards for Hazardous Air Pollutants (RICE NESHAP).

# RICE NESHAP

- Stationary compression ignition (CI) and spark ignition (SI) engines

## Hazardous air pollutants (HAP) from internal combustion engines

formaldehyde
benzene
acetaldehyde
acrolein
ethylbenzene
2,2,4-trimethylpentane
PAH
naphthalene
methanol
methylene chloride
xylene
toluene
1,3-butadiene
hexane

Deadline 2013 !

# RICE NESHAP -formaldehyde

- For rich burn engines >500 horsepower,
  - RICE NESHAP rule requires
    - >76% formaldehyde removal efficiency
    - or below 2.7ppmv@15% $O_2$.

# How?

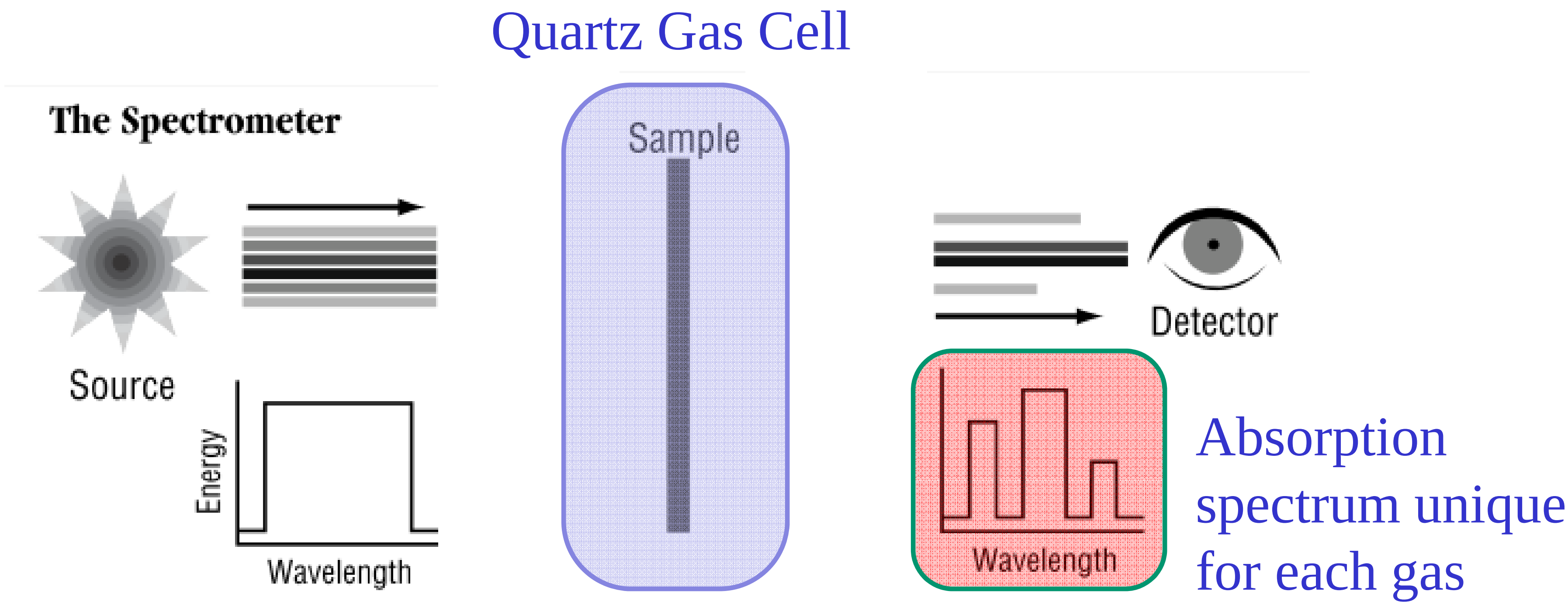
- EPA proposes using EPA Method 320 or ASTM D6348-03 for formaldehyde measurements.
  - Both use Fourier Transform Infrared Spectrometer (FTIR).
- Alternative:
  - EPA Method 323

# FTIR advantages

- FTIR is cost-effective if more than 4 gases need to be measured.
- FTIR requires minimum calibration and so reduces costs.
- Can be easily shipped on-site.

# How does FTIR work?

- Fourier Transform Infrared Spectroscopy
  - Qualitative and quantitative




FTIR instrument includes analysis software, calibration library

# Objective

- To describe issues and challenges of using FTIR for formaldehyde ($CH_2O$) measurement.
- To investigate how accurate low formaldehyde measurement is, with different instrument settings and the presence of other exhaust chemical components.

# Experimental - Test parameters

- Instrument setup
  - Use FTIR manufacturer's recommended specs
    - Gas cell pressure, line position, spectral resolution, path length, etc.
    - Gas cell temperature
      - Method of 150°C (302°F) vs. 191°C (375.8°F) gas cell temperature.
      - MKS recommends using 191°C cell temperature however, some companies in the field use the 150°C method (older).

Tested in this paper

# Experimental - Test parameters (Cont’d)

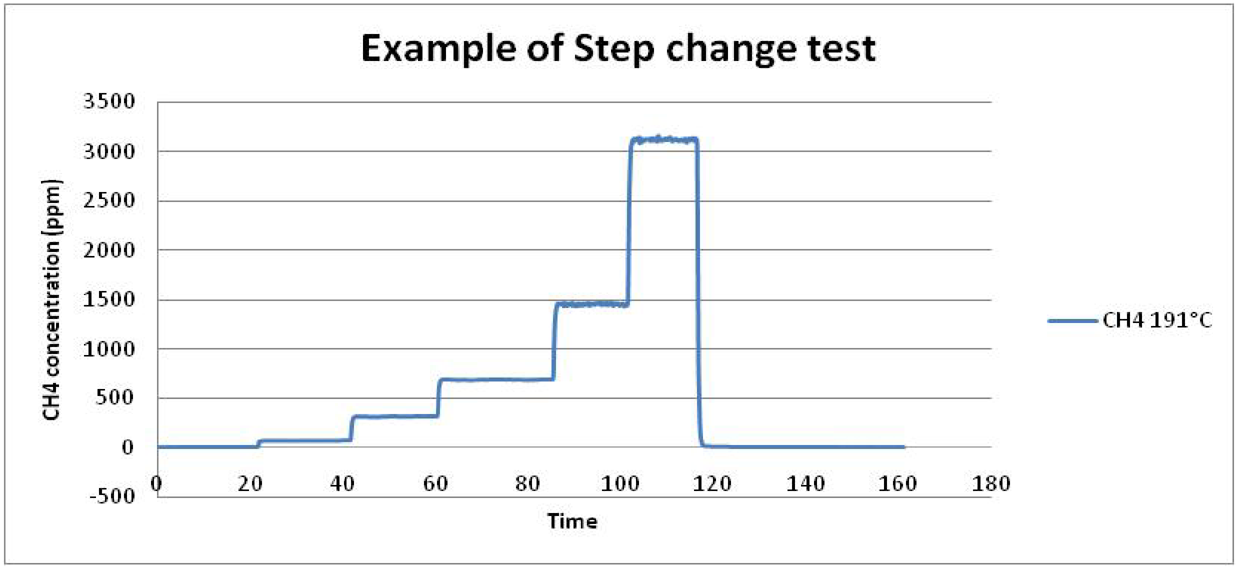
- Exhaust chemical components
  - Methane ($CH_4$)
  - Ethane ($C_2H_6$)
  - Formaldehyde ($CH_2O$)
  - Nitric oxides (NOx)
  - Carbon monoixde (CO)
  - Carbon dioxide ($CO_2$)
  - Water ($H_2O$)

Tested in this paper

# Test Procedures

Equipment: model gas reactor, mass flow controllers, bottled gases, preheater, heating tape, FTIR

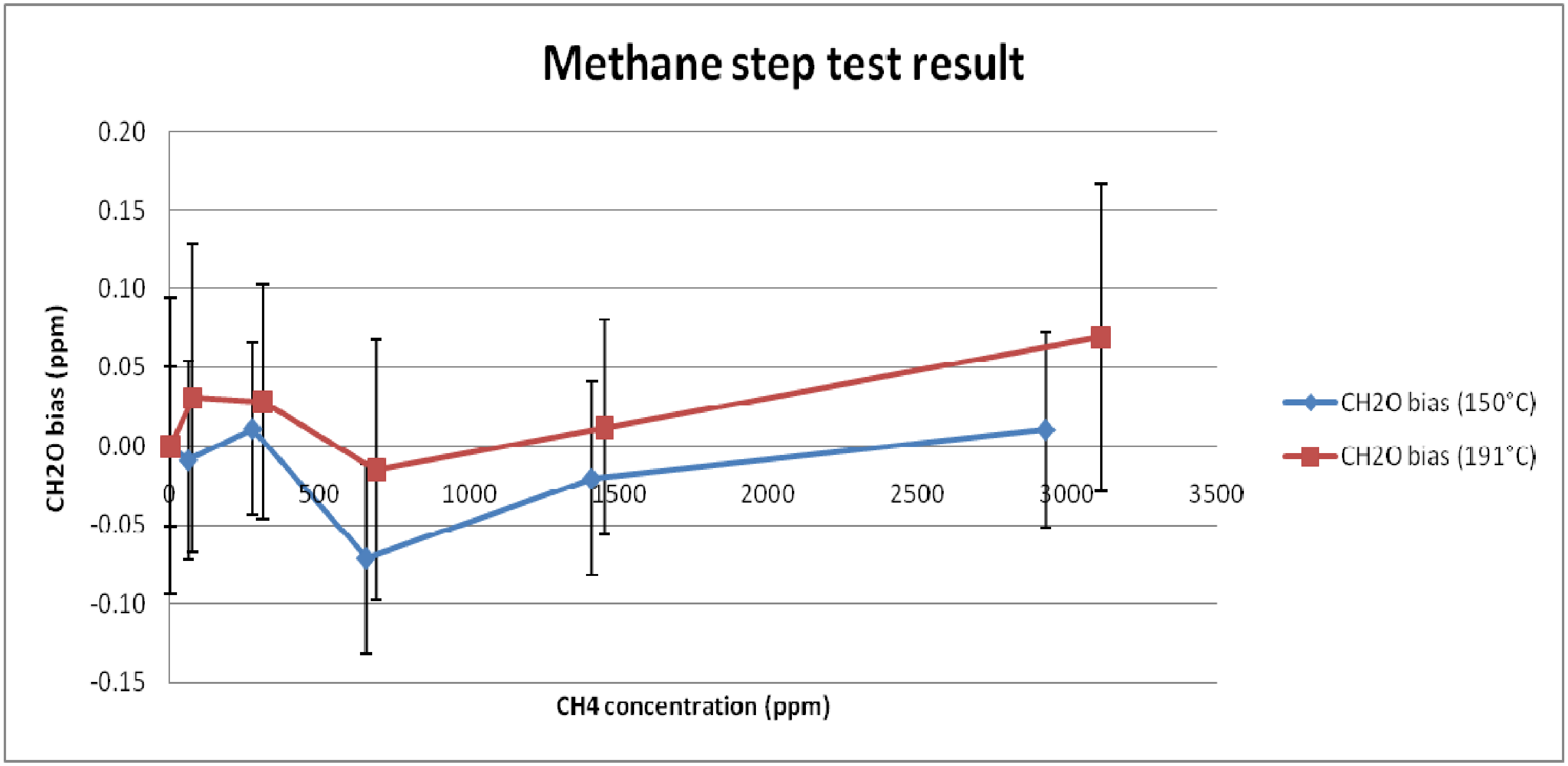
1. Base stream: $N_2$ + air
2. Add in desired gas components (e.g. methane) as step change.
3. Step change at difference concentrations.
4. Repeat test with different gas cell temperatures.



# 1. FIXED $N_2$ + AIR, 0 PPM $CH_2O$ STEP TEST ON METHANE

# No bias with methane!

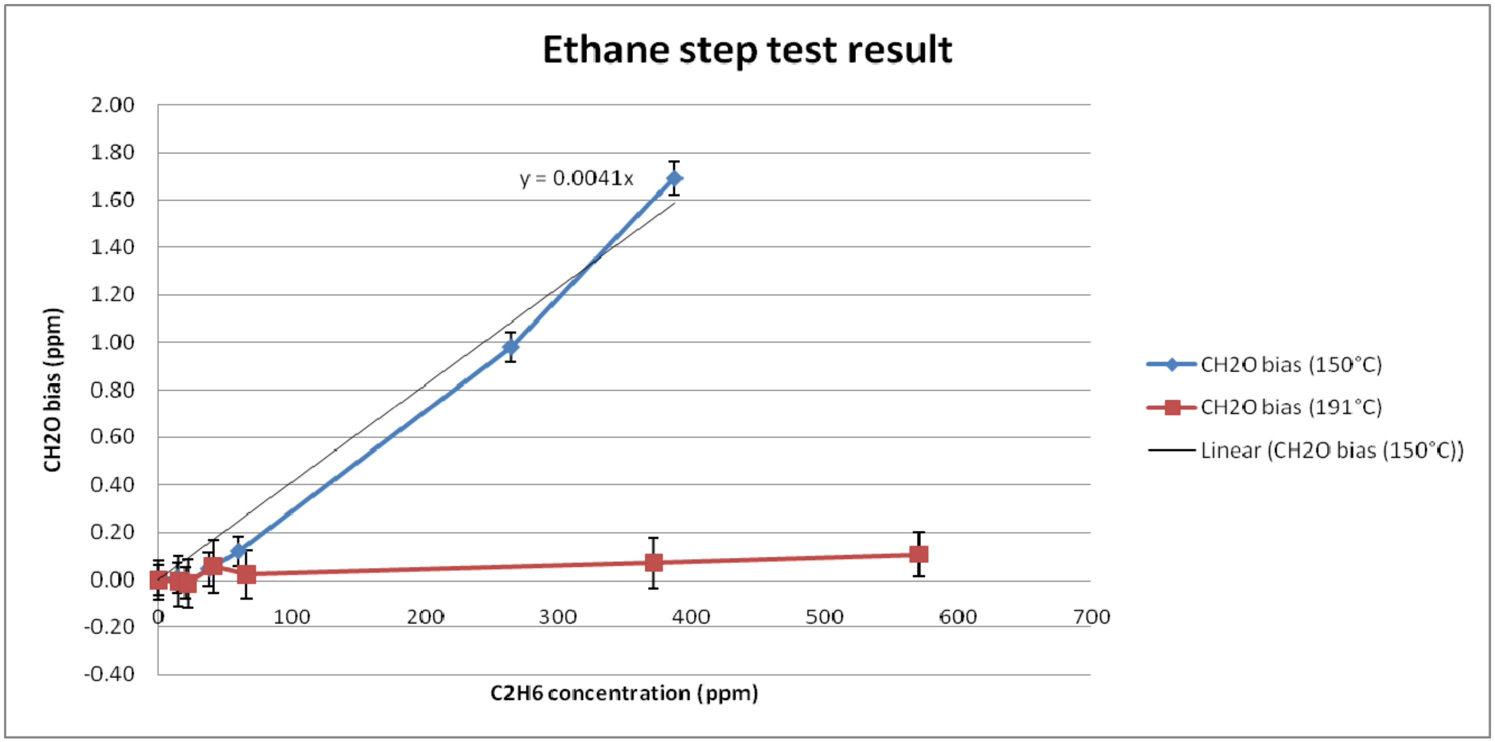
- Within the FTIR detection limit of 0.3ppm $CH_2O$ and the standard deviation; no significant bias on $CH_2O$ readings:



# 2. FIXED $N_2$ + AIR, 0 PPM $CH_2O$ STEP TEST ON ETHANE

# Ethane causes bias!

- 150°C cell temperature method,
  - $[CH_2O \text{ bias}] = 0.004[C_2H_6]$
- 191°C cell temperature method,
  - formaldehyde bias is within the FTIR detection limit of 0.3ppm



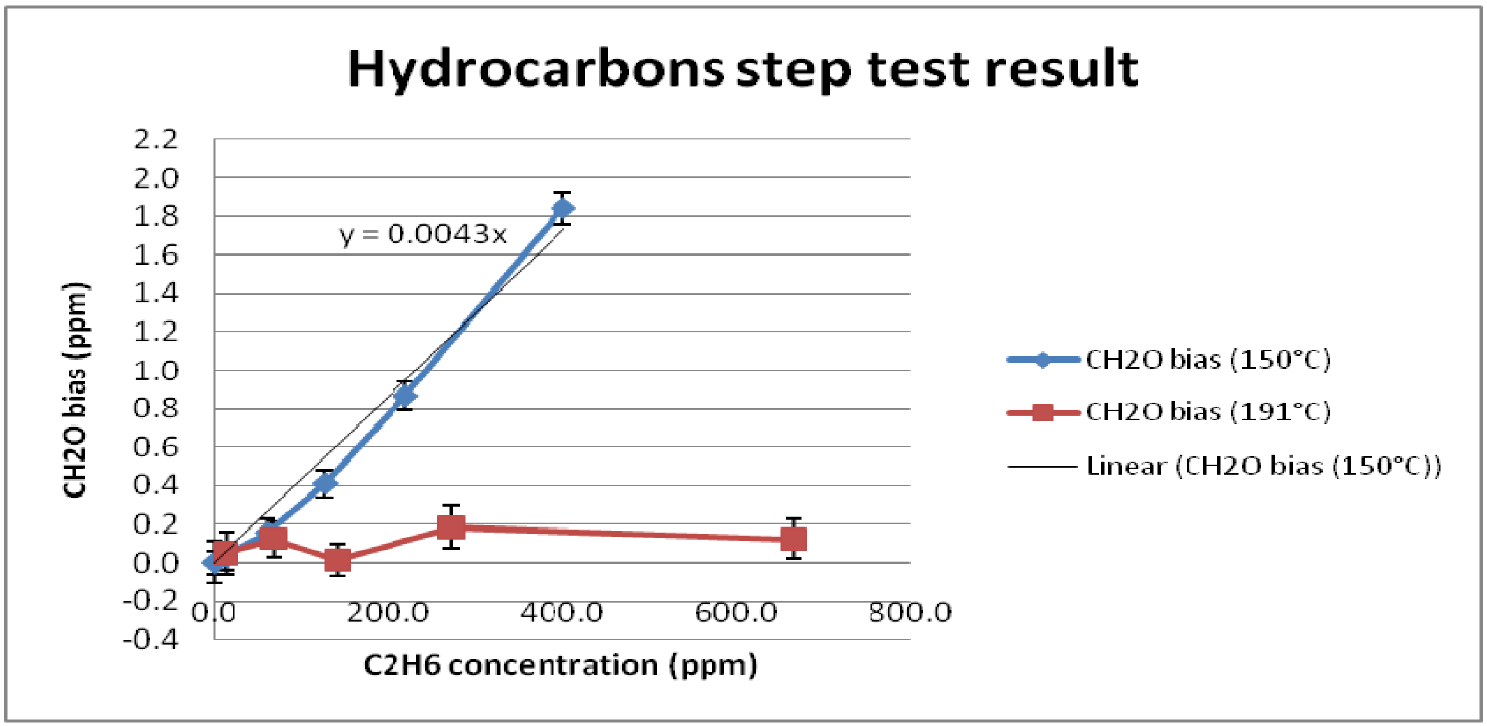
# 3. FIXED $N_2$ + AIR, 0PPM $CH_2O$ STEP TEST ON HC MIXTURE

**(HC MIXTURE OF 2% PROPANE, 6% ETHANE,**

**40% METHANE)**

# Other hydrocarbons?

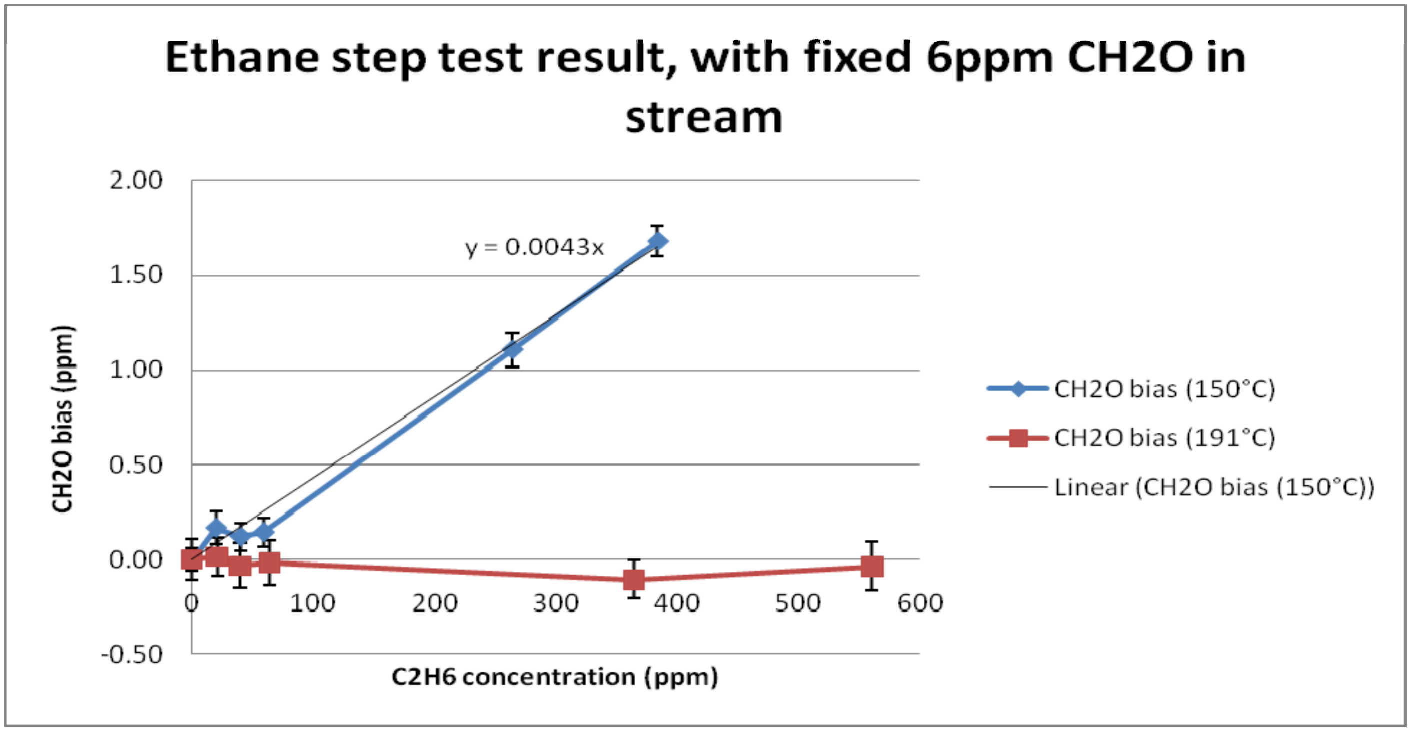
- Consistent with $C_2H_6$ test results:
  - $[CH_2O \text{ bias}] = 0.004 [C_2H_6]$ for the 150 °C method
  - No significant bias when using the 191°C method



# 4. FIXED $N_2$ + AIR + 6PPM $CH_2O$, STEP TEST ON ETHANE

# Ethane + formaldehyde?

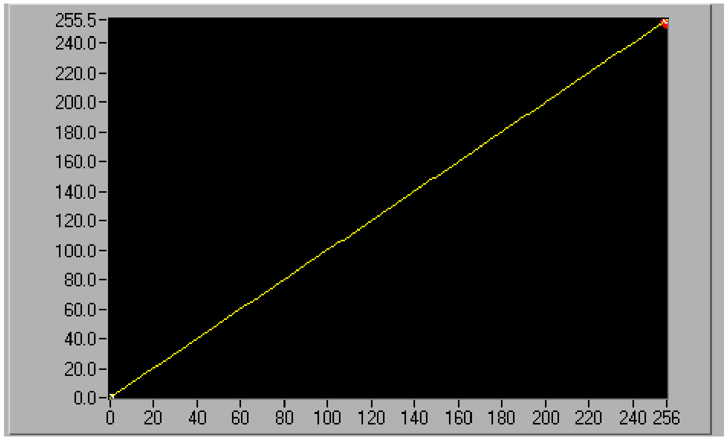
- Consistent with $C_2H_6$ test results:
  - [$CH_2O$ bias] = 0.004 [$C_2H_6$] for the 150°C method
  - No significant bias when using the 191°C method.



# Bias by ethane – Why?

- Bias of formaldehyde by ethane is caused by the incapability of the 150°C cell temp ethane calibration file to match sufficiently well with the spectra of higher concentration of ethane.

Single point (0-50ppm):
- Measurements higher than 50ppm are calculated by extrapolation.




Please see detail proofs in paper.

# Field test examples

- Formaldehyde and ethane data:

**Fail the criterion of 76% formaldehyde removal efficiency**

| Formaldehyde | | | | | |
|---|---|---|---|---|---|
| Engine # | 1 | 2 | 3 | 4 | 5 |
| Catalyst Outlet (ppm) | 5.3 | 1.3 | 0.6 | 0.4 | 0.5 |
| Engine Outlet (ppm) | 19.1 | 5 | 4.2 | 6.6 | 6.9 |
| % conv. | 72.3 | 74.0 | 85.7 | 93.9 | 92.8 |

| Ethane | | | | | |
|---|---|---|---|---|---|
| Catalyst Outlet (ppm) | 459.2 | 30 | 50.0 | 44.7 | 23.3 |
| Engine Outlet (ppm) | 703.6 | 80 | 140.1 | 70.1 | 114.9 |

$CH_2O$ conversion without bias adjustment .

# Pass or fail?

- If [$CH_2O$ bias] = 0.004 [$C_2H_6$] is taken into account:

| (at 150°C gas cell temperature) | Ethane | Formaldehyde | Formaldehyde **(correct for bias)** |
|---|---|---|---|
| Engine outlet (ppm) | 703.6 | 19.1 | 16.22 |
| Catalyst outlet (ppm) | 459.2 | 5.3 | 3.42 |
| Conversion % | | 72.3% | **78.9%** |

**With bias = Fail**

**Corrected for bias = Pass**

# Implications of results on field testing

- Issue in emission test
  - especially at low $CH_2O$ conc. (<10 ppm), or high ethane conc. situations
  - The effect would be most noticeable when the $CH_2O$ value is close to the passing target of >76% formaldehyde removal efficiency or 2.7ppmv (@15%$O_2$).

# Conclusion

- EPA Method 320 and ASTM D6348-03 provides sufficient precision/accuracy for $CH_2O$ in RICE NESHAP rule when ethane bias is eliminated.
  - Correct sampling methodologies must be followed
  - However, tighter regulations may require a new test methodology.
- MKS 2030 FTIR:
  - Method of gas cell temp. 191°C eliminates ethane bias
  - Method of gas cell temp. 150°C not recommended.

# Thank you!


DCL International Inc
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