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

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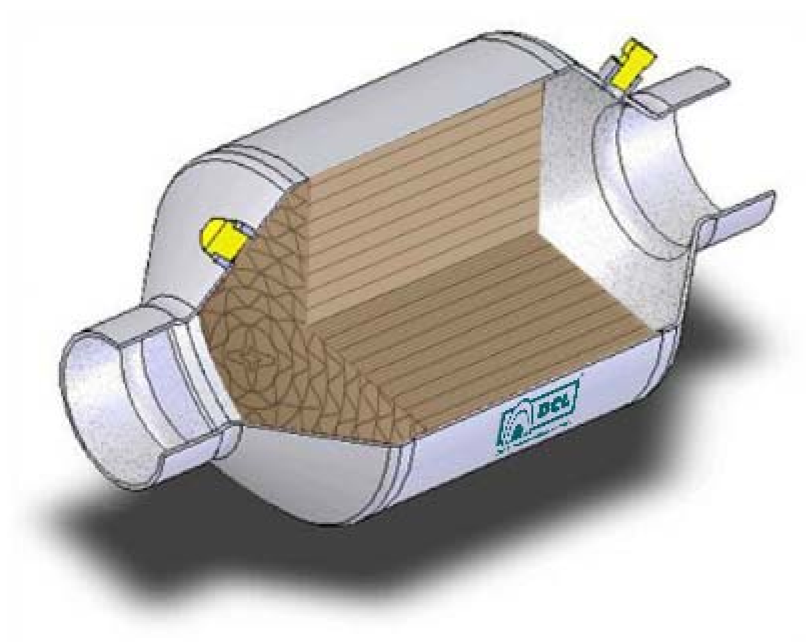
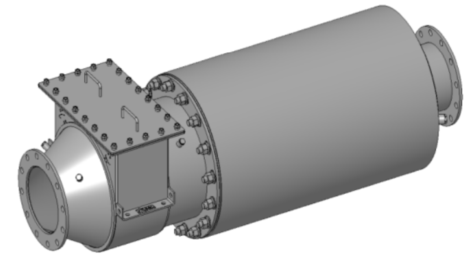
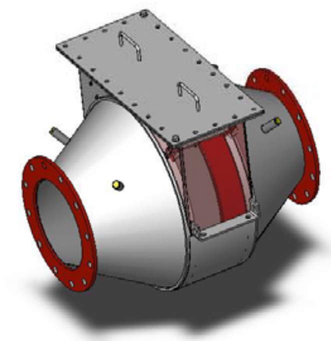
Company: DCL International Inc.

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

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

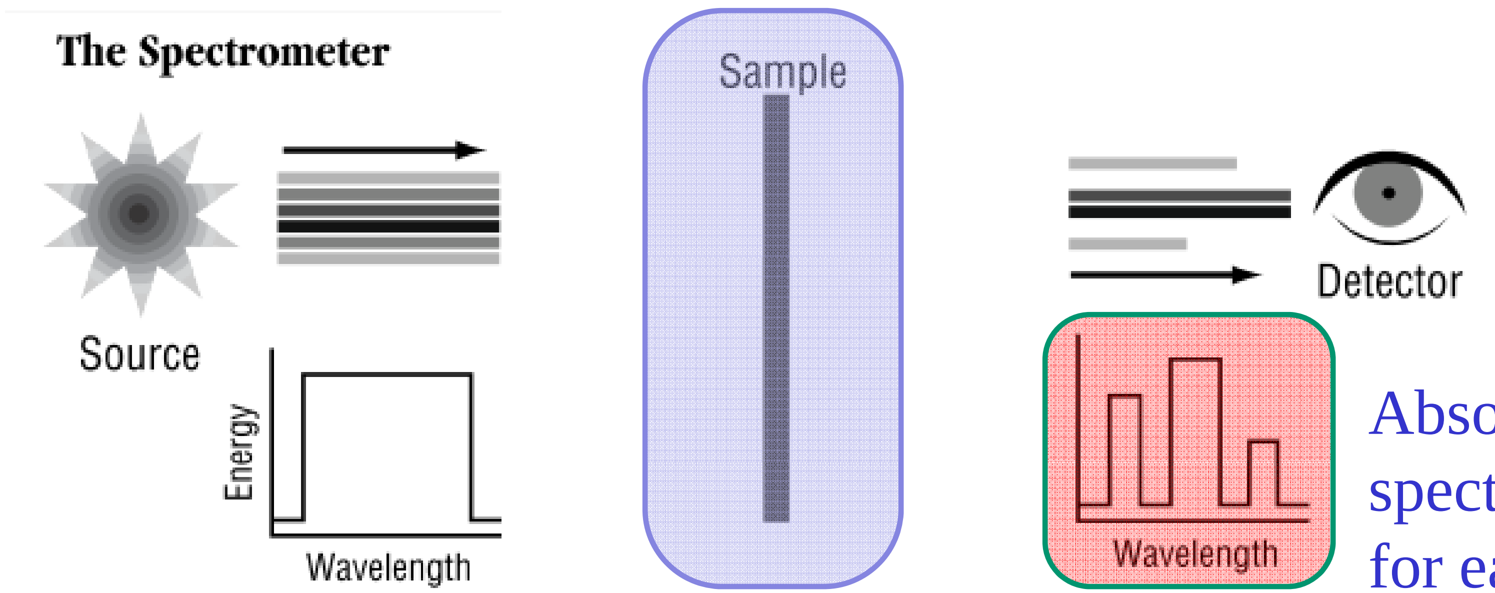
FTIR advantages

- 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

Quartz Gas Cell



Absorption spectrum unique for each gas

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)

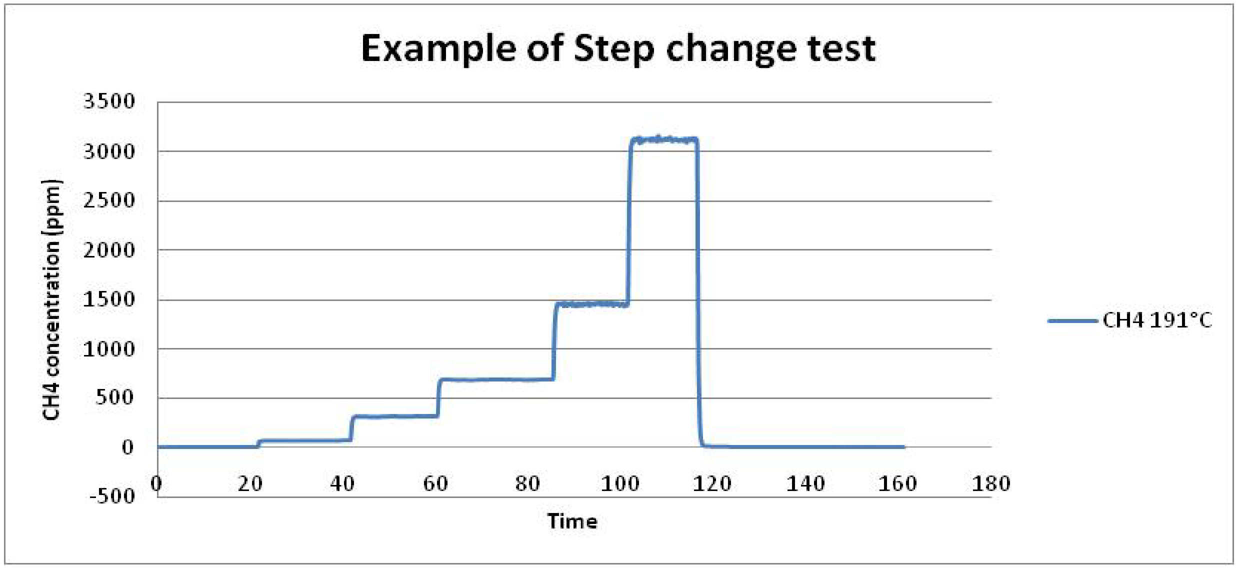
- Exhaust chemical components
  - Methane (CH_4)
  - Ethane (C_2H_6)
  - Formaldehyde (CH_2O)
  - Nitric oxides (NOx)
  - Carbon monoixde (CO)
  - Carbon dioxide (CO_2)
  - Water (H_2O)

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.



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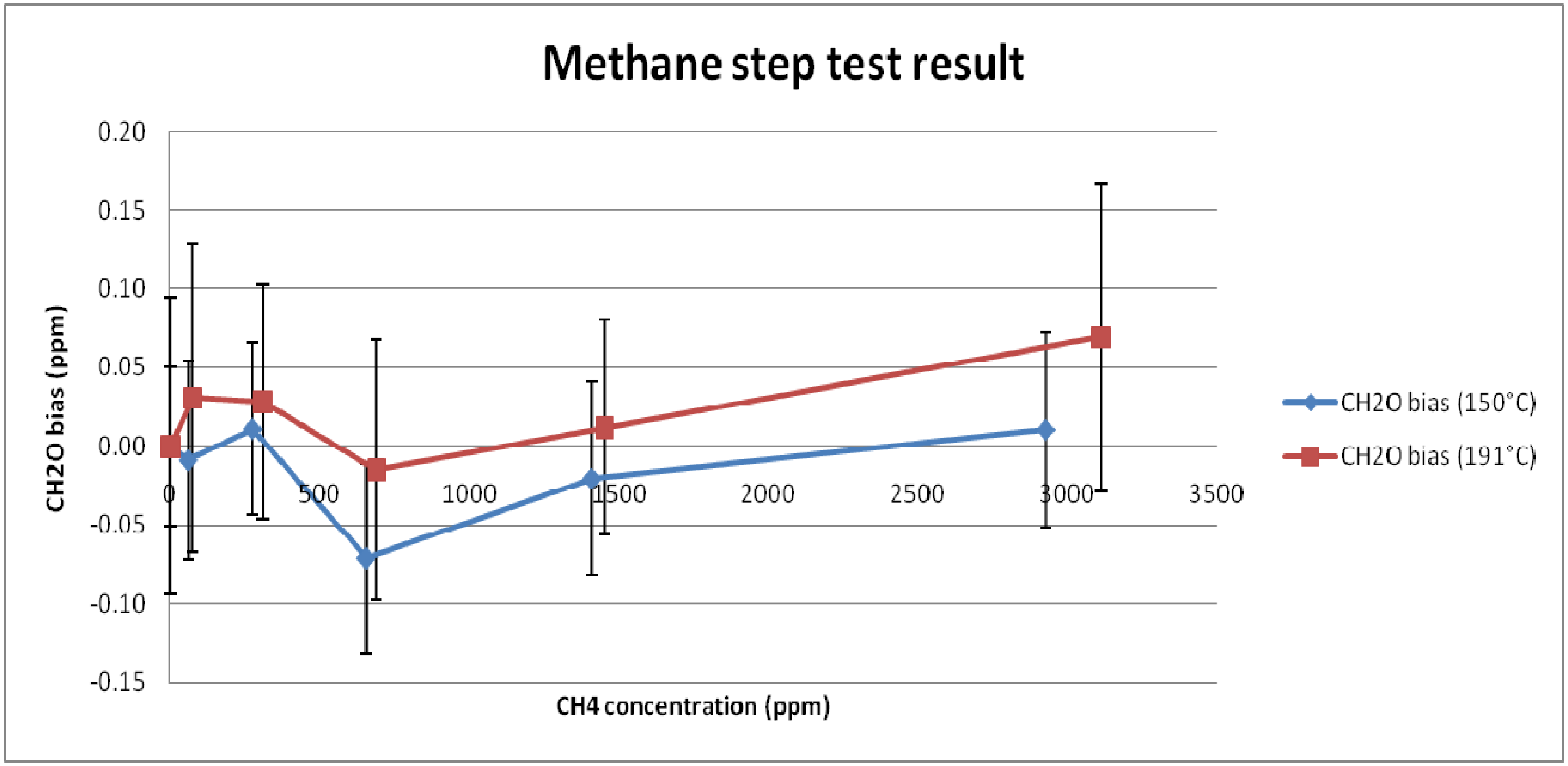
1. FIXED N_2 + AIR, 0 PPM CH_2O STEP TEST ON METHANE

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:



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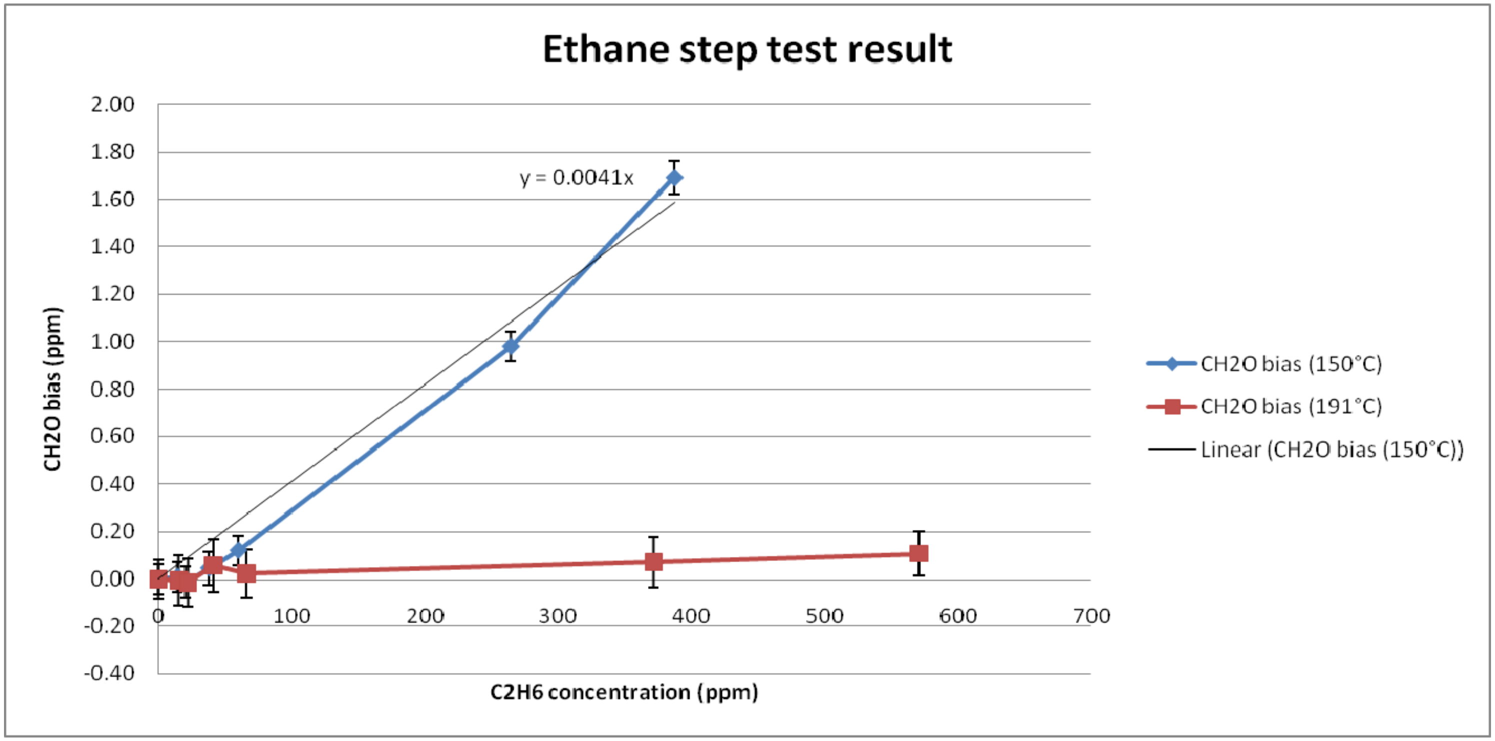
2. FIXED N_2 + AIR, 0 PPM CH_2O STEP TEST ON ETHANE

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



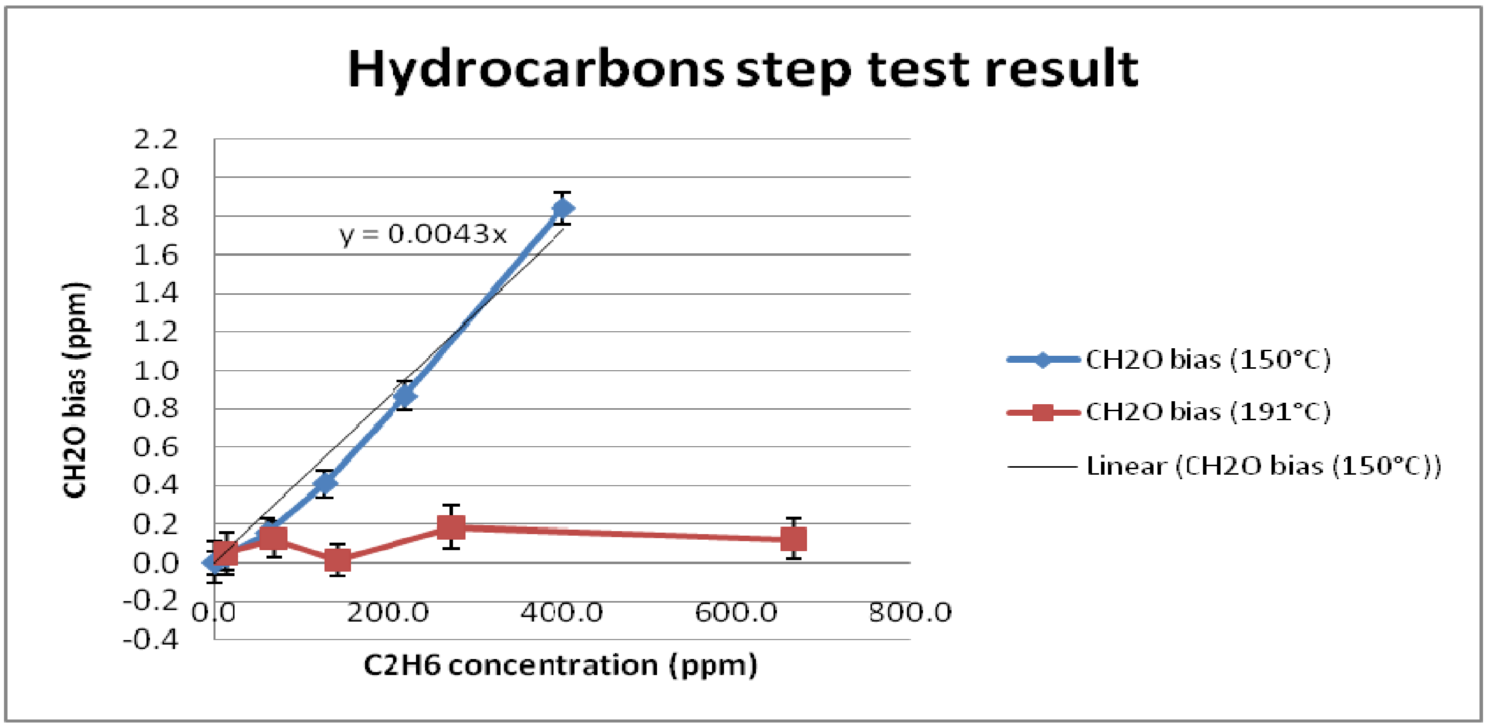
3. FIXED N_2 + AIR, 0PPM CH_2O
STEP TEST ON HC MIXTURE

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

40% METHANE)

Other hydrocarbons?

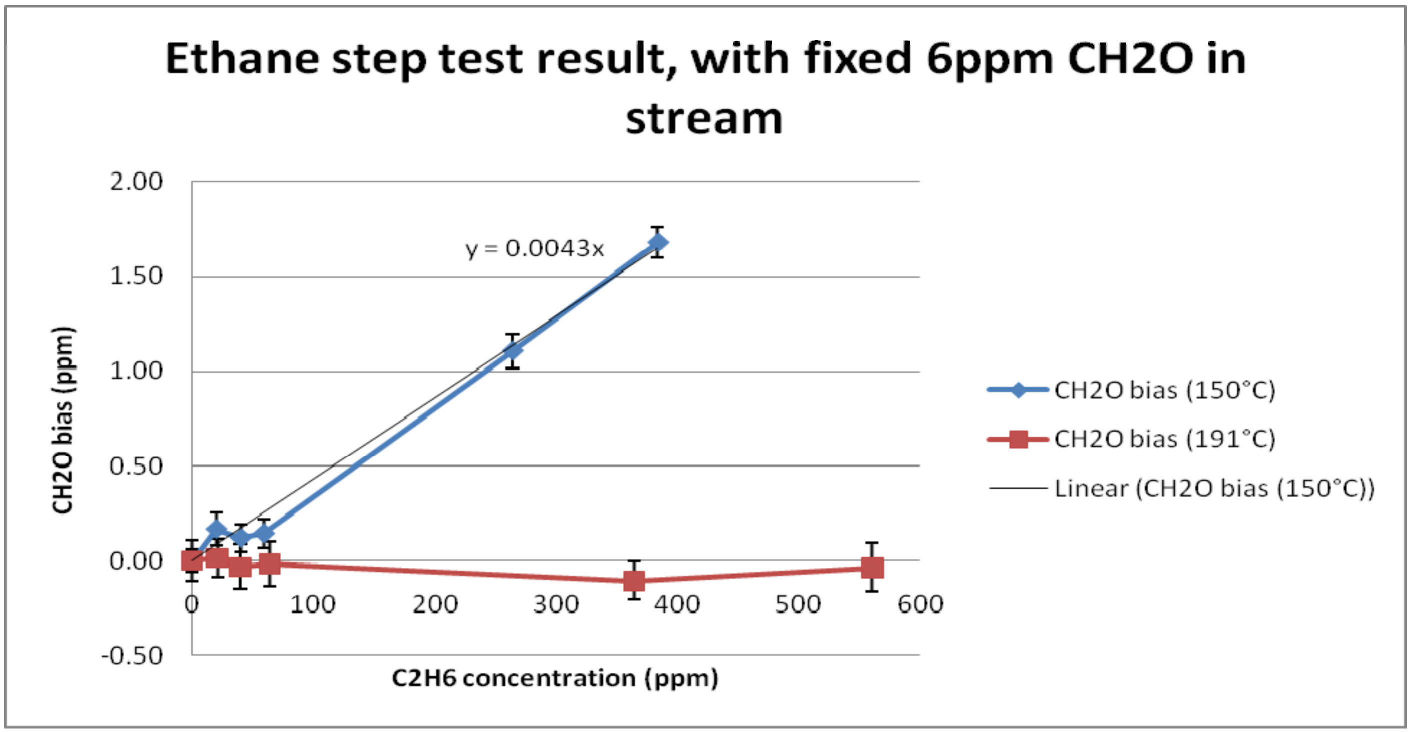
- Consistent with C_2H_6 test results:
  - [CH_2O bias] = 0.004 [C_2H_6] for the 150 °C method
  - No significant bias when using the 191˚C method



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

Ethane + formaldehyde?

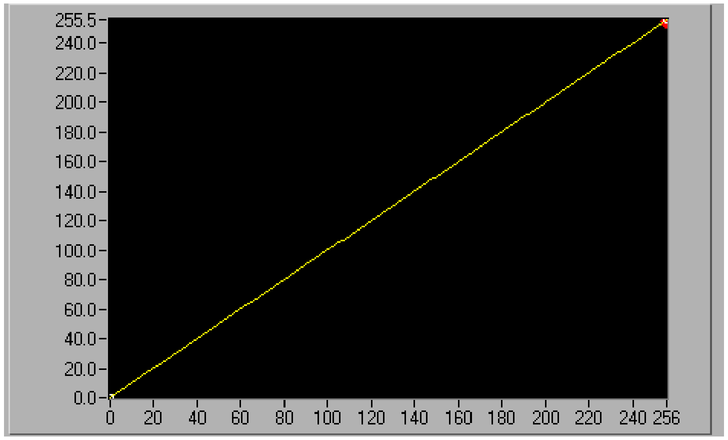
- Consistent with C_2H_6 test results:
  - [CH_2O bias] = 0.004 [C_2H_6] for the 150°C method
  - No significant bias when using the 191°C method.



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:

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

Fail the criterion of 76% formaldehyde removal efficiency

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
Global Leader in Emission Control Solutions