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

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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.
RICE NESHAAP

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

Hazardous air pollutants (HAP) from internal combustion engines

Deadline 2013!
RICE NESHAP - formaldehyde

- For rich burn engines >500 horsepower,
  - RICE NESHAP rule requires
    - >76% formaldehyde removal efficiency
    - or below 2.7 ppmv@15% O₂.
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

FTIR instrument includes analysis software, calibration library
Objective

- To describe issues and challenges of using FTIR for formaldehyde (CH$_2$O) 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.

Tested in this paper
  – MKS recommends using 191°C cell temperature however, some companies in the field use the 150°C method (older).
Experimental - Test parameters (Cont’d)

- Exhaust chemical components
  - Methane (CH\textsubscript{4})
  - Ethane (C\textsubscript{2}H\textsubscript{6})
  - Formaldehyde (CH\textsubscript{2}O)
    - Nitric oxides (NO\textsubscript{x})
    - Carbon monoixde (CO)
    - Carbon dioxide (CO\textsubscript{2})
    - Water (H\textsubscript{2}O)

Tested in this paper
Test Procedures

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

1. Base stream: $\text{N}_2 + \text{air}$
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.

Example of Step change test
1. FIXED $\text{N}_2 + \text{AIR}, 0$ PPM $\text{CH}_2\text{O}$
STEP TEST ON METHANE
No bias with methane!

- Within the FTIR detection limit of 0.3ppm CH$_2$O and the standard deviation; no significant bias on CH$_2$O readings:
2. FIXED $N_2$ + AIR, 0 PPM CH$_2$O
STEP TEST ON ETHANE
Ethane causes bias!

- $150^\circ C$ cell temperature method,
  - $[\text{CH}_2\text{O bias}] = 0.004[\text{C}_2\text{H}_6]$  
- $191^\circ C$ cell temperature method,
  - formaldehyde bias is within the FTIR detection limit of 0.3ppm
3. FIXED N₂ + AIR, 0PPM CH₂O
STEP TEST ON HC MIXTURE

(HC MIXTURE OF 2% PROPANE, 6% ETHANE,
40% METHANE)
Other hydrocarbons?

- Consistent with \( \text{C}_2\text{H}_6 \) test results:
  - \([\text{CH}_2\text{O \ bias}] = 0.004 \ [\text{C}_2\text{H}_6] \) for the 150 \(^{\circ}\) C method
  - No significant bias when using the 191\(^{\circ}\)C method
4. FIXED $N_2 + \text{AIR} + 6\text{PPM CH}_2\text{O}$, STEP TEST ON ETHANE
Ethane + formaldehyde?

- 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.
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:

<table>
<thead>
<tr>
<th>Formaldehyde</th>
<th>Engine #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine #</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Catalyst Outlet (ppm)</td>
<td>5.3</td>
<td>1.3</td>
<td>0.6</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Engine Outlet (ppm)</td>
<td>19.1</td>
<td>5</td>
<td>4.2</td>
<td>6.6</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>% conv.</td>
<td>72.3</td>
<td>74.0</td>
<td>85.7</td>
<td>93.9</td>
<td>92.8</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ethane</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Outlet (ppm)</td>
<td>459.2</td>
<td>30</td>
<td>50.0</td>
<td>44.7</td>
<td>23.3</td>
</tr>
<tr>
<td>Engine Outlet (ppm)</td>
<td>703.6</td>
<td>80</td>
<td>140.1</td>
<td>70.1</td>
<td>114.9</td>
</tr>
</tbody>
</table>

Fail the criterion of 76% formaldehyde removal efficiency. CH₂O conversion without bias adjustment.
Pass or fail?

- If $[\text{CH}_2\text{O \ bias}] = 0.004 [\text{C}_2\text{H}_6]$ is taken into account:

<table>
<thead>
<tr>
<th></th>
<th>Ethane (at 150°C gas cell temperature)</th>
<th>Formaldehyde</th>
<th>Formaldehyde (correct for bias)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine outlet (ppm)</td>
<td>703.6</td>
<td>19.1</td>
<td>16.22</td>
</tr>
<tr>
<td>Catalyst outlet (ppm)</td>
<td>459.2</td>
<td>5.3</td>
<td>3.42</td>
</tr>
<tr>
<td>Conversion %</td>
<td>72.3%</td>
<td>78.9%</td>
<td></td>
</tr>
</tbody>
</table>

With bias = Fail
Corrected for bias = Pass
Implications of results on field testing

- Issue in emission test
  - especially at low CH$_2$O conc. (<10 ppm), or high ethane conc. situations
  - The effect would be most noticeable when the CH$_2$O 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$_2$O 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!