Certification Methods Errors in the Analysis of NMHC and VOCs in CNG-Based Engine Emissions

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Presented at EPA Region 6 - 25th Annual Quality Assurance Conference
October 21st, 2015
Which is Best for CNG Fueled Engine NMHC or VOCs Emissions?

- FID
- FTIR
- GC
EPA Proposed Changes to 40 CFR Subpart JJJJ

- Rule as proposed has Method 25A along with EPA part 1065 for NMC providing VOCs
  - (v.) Not correct – NMC only provides CH4, **NOT** Ethane gives NMHC not VOCs

### Current Regulation since 2008

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- Rule as proposed has Method 25A along with EPA part 1065 for NMC providing VOCs
  - (v.) Not correct – NMC only provides CH₄, **NOT** Ethane gives NMHC not VOCs
  - (vi.) Not correct – Methane and Ethane **ARE** needed for VOCs
  - EPA clarified - M320/ASTM D6348 and Method 18 are required for VOCs but proposed language is written incorrectly.

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EPA Proposed Changes to 40 CFR Subpart JJJJ

“EPA clarification comments on Sept 28 explaining why this step is being considered has many flaws”

- A speciated list of gaseous components that are always present in these types of engines is available with validation provided.
  - The community of stack testers and vehicle and engine manufacturers have numerous data sets comparing speciated FTIR methods to Method 25A
  - Numerous published data sets on LD Vehicles comparing different fuel types to THC-FIDs are also available
  - 3 - 7 components account for more than 95% of the VOCs in Lean burn, Rich burn and 2-stroke engines

<table>
<thead>
<tr>
<th>20 JHHI Data Sets</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Butane</th>
<th>Ethylene</th>
<th>Propylene</th>
<th>Acetylene</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Methanol</th>
<th>Formic Acid</th>
<th>m-xylene</th>
<th>1,3-butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average for Specie</td>
<td>1085.44</td>
<td>55.72</td>
<td>6.75</td>
<td>2.95</td>
<td>7.39</td>
<td>1.10</td>
<td>0.21</td>
<td>13.01</td>
<td>0.21</td>
<td>0.51</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>Median For Specie</td>
<td>871.00</td>
<td>59.76</td>
<td>4.32</td>
<td>2.65</td>
<td>6.37</td>
<td>0.74</td>
<td>0.00</td>
<td>8.46</td>
<td>0.00</td>
<td>0.20</td>
<td>0.09</td>
<td>0.00</td>
<td>0.15</td>
</tr>
</tbody>
</table>

- FTIR methods VOC ARE robust enough for Total VOCs
  - QA/QC checks are spelled out in M320 and D6348 checking interference
  - Error of the Difference method for high methane emissions greatly exceeds that of any speciated method

- There are numerous training opportunities on the use of FTIR that have been offered (and taken up) by state regulators and EPA
Difference Method for NMHC (or VOC)
Direct Method VOC (or NMHC)
Let’s Examine the Various Methods

Difference Method

THC
- FID Method 25A
- Non-CH4 Cutter NMC - FID Part 1065

CH4
- GC-FID, GC-FTIR, GC-MS Method 18
- FTIR Method 320 ASTM D6348

NMHC (THC – CH4)

VOC (NMHC – C2H6)

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Method 25A THC Analysis

- Gas sample extracted from source through heated sample line and glass fiber filter and sent to a flame ionization analyzer (FIA)
  - Sampling components to FIA shall be heated $\geq 110^\circ\text{C}$
  - FIA shall be heated $\geq 120^\circ\text{C}$
  - Heavy HCs must be heated to 190$^\circ\text{C}$ to not condense

- Calibration of FIA
  - Use Certified Gases which were certified by the EPA Protocol method - Should use 2% or better accuracy
  - SPAN the analyzer using highest span gas (85-90% FIA range)
    - Check response of mid and low range gas cylinder
    - Must be <5% of calibration gas value
  - Zero Drift
    - Must be $\pm 3\%$ of Span value
Method 25A Using Single FID with NMC for NMHC
EPA Part 1065.365 (e) or (f)

- Span FID THC to $C_3H_8$ on C1 basis
- Run CH4 through Bypass NMC then NMC
  - Max C1 Range concentration
  - $P_{\text{FCH}_4[\text{NMC-FID}]} = \frac{\text{CH}_4\text{NMC}}{\text{CH}_4\text{Bypass}}$
Method 25A Using Single FID with NMC for NMHC
EPA Part 1065.365 (e) or (f)

- Run Ethane through NMC and Bypass
- Expected NMHC max
- \[ PF_{C_2H_6[NMC-FID]} = \frac{C_2H_6_{NMHC}}{C_2H_6_{Bypass}} \]
Field Sampling

- Sample is switched from going straight to FID (Valve1) to going through the NMC (Valve2)
- Depending on how you calibrate and use the FID with NMC the NMHC Equations are different
Example Calculation of NMHC
Part 1065.660(b)(2)(ii)

\[
x_{NMHC} = \frac{x_{THC[THC-FID]cor} \cdot PF_{CH4[NMC-FID]} - x_{THC[NMC-FID]cor}}{PF_{CH4[NMC-FID]} - PF_{C2H6[NMC-FID]}}
\]

- \( X_{NMHC} \) : NMHC concentration
- \( X_{THC[THC-FID]cor} \) : Sample THC corrected to dry on THC-FID
- \( PF_{CH4[NMC-FID]} \) : NMC CH4 penetration fraction
- \( X_{THC[NMC-FID]cor} \) : Sample THC corrected to dry on THC-FID through NMC
- \( PF_{C2H6[NMC-FID]} \) : NMC Ethane penetration fraction

(1) Large number THC-FID (THC) minus another Large number NMC-FID (CH4)
(2) Plus Tester do not do this calculation – they use the numbers from the Analyzer for NMHC – NOT corrected for the penetration factors
So Does the FTIR Work?

Difference Method

THC
- FID Method 25A
  - Non-CH4 Cutter NMC Part 1065
    - FID Part 1065
    - NMHC (THC – CH4)

CH4
- GC-FID, GC-FTIR, GC-MS Method 18
  - FTIR Method 320 ASTM D6348
  - VOC (NMHC – C2H6)
Method 320 or D6348  
Fourier Transform Infrared (FTIR) Spectroscopy

- Based on IR light absorption
  - Energy (IR radiation) heats the gas molecule - vibrates and rotates
  - The result is a pattern and peak height which correlates to the gas molecule and concentration
  - Gas molecule must have a dipole moment
    - $\text{O}_2$, $\text{H}_2$, $\text{N}_2$, $\text{Ar}$, $\text{He}$ do NOT have a dipole moment
Interferogram to Gas Concentration Pathway

- Interferogram
- Single Beam Absorbance Spectrum
- Method Analysis

Fourier Transform Algorithm

\[ I(\tilde{v}) = \int_{-\infty}^{+\infty} I(x)D(\tilde{v}) \exp(2\pi\tilde{v}x) \, dx \]

Remove Background

\[ A = -\log(I/I_0) \]

Spectrum Analysis

- Method Determination (Gas, Diesel, CNG, Etc.)
- Analysis of absorption regions
- Speciation of gases
Background and Sample Single Beam Spectra

BACKGROUND (Io) N₂ Purge

SAMPLE (I) 1000 ppm NH₃
Final Absorbance Spectrum Proportional to Concentration

1000 ppm NH₃

Ethanol 1000 ppm

Ethanol 500 ppm
10 Typical Components (50 ppm-v Conc)

Different peak heights for same concentrations

- CO₂
- CO
CNG Emission Spectrum
~10% H₂O, 1000 ppm CH₄
CNG Emission Spectrum
~10% H₂O, 1000 ppm CH₄
Resolution
Low Resolution (2.0 cm\(^{-1}\))

Example of catalyst performance evaluation
Figure used with permission from Johnson Matthey plc, Wayne, PA
Resolution
High Resolution (0.5 cm$^{-1}$)

Example of catalyst performance evaluation
Figure used with permission from Johnson Matthey plc, Wayne, PA
Interference Removal
Masking and Removing \text{H}_2\text{O} \text{ Interference}

WHITE: Sample spectrum (~150ppm NO)
RED: 35\% \text{H}_2\text{O} calibration spectrum

WHITE: Sample spectrum (minus \text{H}2\text{O})
GREEN: 150ppm NO calibration spectrum
Review of Difference Method Errors

Difference Method

THC
- FID Method 25A

Non-CH4 Cutter
- NMC Part 1065
- FID Part 1065

NMHC (THC – CH4)

CH4
- GC-FID, GC-FTIR, GC-MS Method 18
- FTIR Method 320 ASTM D6348

VOC (NMHC – C2H6)
## FID and FTIR Comparison of THC and CH4 values

### THC %Error

<table>
<thead>
<tr>
<th>Mode</th>
<th>THC FID</th>
<th>THC FTIR</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine1 Mode 1</td>
<td>847.0</td>
<td>805.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Engine1 Mode 2</td>
<td>1407.9</td>
<td>1328.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Engine1 Mode 3</td>
<td>1795.3</td>
<td>1757.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Engine1 Mode 4</td>
<td>2079.9</td>
<td>2073.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Engine1 Mode 5</td>
<td>2700.5</td>
<td>2679.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

### CH4 NMC %Error

<table>
<thead>
<tr>
<th>Fuel</th>
<th>CH4 NMC FID</th>
<th>CH4 NMC FTIR</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine2 Fuel 1</td>
<td>4420.90</td>
<td>4466.104</td>
<td>1.0</td>
</tr>
<tr>
<td>Engine2 Fuel 2</td>
<td>3297.00</td>
<td>3263.163</td>
<td>1.0</td>
</tr>
<tr>
<td>Engine2 Fuel 3</td>
<td>955.56</td>
<td>924.8726</td>
<td>3.2</td>
</tr>
<tr>
<td>Engine2 Fuel 4</td>
<td>648.53</td>
<td>625.2356</td>
<td>3.6</td>
</tr>
</tbody>
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### CH4 %Error

<table>
<thead>
<tr>
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<th>CH4 FID</th>
<th>CH4 FTIR</th>
<th>%Error</th>
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</thead>
<tbody>
<tr>
<td>Engine1 Mode 1</td>
<td>688.6</td>
<td>687.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Engine1 Mode 2</td>
<td>1181.0</td>
<td>1181.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Engine1 Mode 3</td>
<td>1521.0</td>
<td>1581.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Engine1 Mode 4</td>
<td>1774.7</td>
<td>1888.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Engine1 Mode 5</td>
<td>2320.4</td>
<td>2452.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

**All FTIR values are well within 10% of the FID values**
Growth of the Random Error using the Difference Method

\[ \frac{\sigma_D}{D} = \left[ \left( \frac{A}{D} \right)^2 \cdot \left( \frac{\sigma_A}{A} \right)^2 + \left( \frac{B}{D} \right)^2 \cdot \left( \frac{\sigma_B}{B} \right)^2 \right]^{\frac{1}{2}} \]

NMHC (D) = THC (A) - CH4 (B)

Analyzer Target Error 5%

Critical Point

Diesel

CNG
Difference versus Direct

- **Difference Method**
  - Uses FID for THC
  - FTIR for CH₄ and C₂H₆
  - Errors are compounded as CH₄ and C₂H₆ reach ~50% of THC

- **Direct or Speciated Method**
  - Uses FTIR only for calculating VOCs
  - Uses fixed list of components in CNG emissions
  - Can add or subtract other components if present
  - Errors are much lower and due to analyzer DLs

- **Validation of Method**
  - Test for VOC interference biases by running 15% H₂O, 10% CO₂, 3000 ppm CH₄ and 100 ppm Ethane through Method
### Speciated CNG Engine Exhaust Emissions

<table>
<thead>
<tr>
<th></th>
<th>LEAN</th>
<th>RICH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Engine #1</td>
<td>Engine #2</td>
</tr>
<tr>
<td><strong>H₂O%</strong></td>
<td>9.6</td>
<td>10.2</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>25.3</td>
<td>14.7</td>
</tr>
<tr>
<td><strong>CO₂%</strong></td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td><strong>CH₄</strong></td>
<td>1618</td>
<td>1851</td>
</tr>
<tr>
<td><strong>ETHANE</strong></td>
<td>20.3</td>
<td>10.5</td>
</tr>
<tr>
<td><strong>ETHYLENE</strong></td>
<td>3.5</td>
<td>4.45</td>
</tr>
<tr>
<td><strong>ACETYLENE</strong></td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td><strong>PROPANE</strong></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>PROPYLENE</strong></td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>BUTANE</strong></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>FORMALDEHYDE</strong></td>
<td>14.2</td>
<td>17.6</td>
</tr>
<tr>
<td><strong>FORMIC ACID</strong></td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td><strong>ACETALDEHYDE</strong></td>
<td>3.26</td>
<td>2.15</td>
</tr>
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The oxygenates are greater than the alkanes – they need to be added.
## Difference FID Method for NMHC Error Estimate

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<tr>
<th></th>
<th>Typical Conc</th>
<th>5% Overall Error (C1)</th>
</tr>
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<tbody>
<tr>
<td>THC</td>
<td>1575 ppm C1</td>
<td>78.9 ppm C1</td>
</tr>
<tr>
<td>CH4</td>
<td>1500 ppm C1</td>
<td>75.0 ppm C1</td>
</tr>
<tr>
<td>NMHC</td>
<td>75 ppm C1</td>
<td>$\sqrt{(78.9^2+75^2)}$± 108.9 ppm(C1) Rel Error = 145%</td>
</tr>
</tbody>
</table>
### Direct FTIR Method for NMHC Error Estimate

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<th>5% Error</th>
<th>Instrument Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ethane</strong></td>
<td>30.0 ppm C1</td>
<td>1.5 ppm C1</td>
<td>1 ppm C1</td>
</tr>
<tr>
<td><strong>Ethylene</strong></td>
<td>10.0 ppm C1</td>
<td>0.5 ppm C1</td>
<td>1 ppm C1</td>
</tr>
<tr>
<td><strong>Acetylene</strong></td>
<td>1.0 ppm C1</td>
<td>0.05 ppm C1</td>
<td>1 ppm C1</td>
</tr>
<tr>
<td><strong>Propylene</strong></td>
<td>1.5 ppm C1</td>
<td>0.08 ppm C1</td>
<td>3 ppm C1</td>
</tr>
<tr>
<td><strong>Propane</strong></td>
<td>3.0 ppm C1</td>
<td>0.15 ppm C1</td>
<td>3 ppm C1</td>
</tr>
<tr>
<td><strong>Butane</strong></td>
<td>2.5 ppm C1</td>
<td>0.13 ppm C1</td>
<td>4 ppm C1</td>
</tr>
<tr>
<td><strong>NMHC</strong></td>
<td>48 ppm C1</td>
<td>$\sqrt{(1.5^2 + 0.5^2 + 0.05^2 + 0.08^2 + 0.15^2 + 0.13^2)}$</td>
<td>$\sqrt{(1^2 + 1^2 + 1^2 + 3^2 + 3^2 + 4^2)}$ ± 5.9 ppm (C1) Rel Error = 12%</td>
</tr>
</tbody>
</table>
Difference vs Direct / Speciated Method Comparing Uncertainties

CH4/THC $>85\%$

CH4/THC $\sim50\%$

Engine Test Number

Engine2 Fuel 1

Engine2 Fuel 2

Engine2 Fuel 3

Engine2 Fuel 4

NMHC (ppmv C1)

<table>
<thead>
<tr>
<th>NMHC (ppmv C1)</th>
<th>Engine2 Fuel 1</th>
<th>Engine2 Fuel 2</th>
<th>Engine2 Fuel 3</th>
<th>Engine2 Fuel 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>THC - CH4 (FID/NMC)</td>
<td>-100</td>
<td>-200</td>
<td>300</td>
<td>-200</td>
</tr>
<tr>
<td>Speciated (FTIR)</td>
<td>100</td>
<td>0</td>
<td>400</td>
<td>0</td>
</tr>
</tbody>
</table>

THC - CH4 (FID/NMC) Speciated (FTIR)
FTIR Can SEE What is in the Emissions for NMHC

Engine 2 Fuel 1

~5ppmC1 Ethylene

~120ppmC1 Ethane
### Stationary Engine Test Example
40 CFR Part 60 JJJJ

<table>
<thead>
<tr>
<th>MAIN COMPONENTS</th>
<th>Engine 1</th>
<th>Engine 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1374 ppm</td>
<td>1618 ppm</td>
</tr>
<tr>
<td>Ethane</td>
<td>24.8 ppm</td>
<td>21.8 ppm</td>
</tr>
<tr>
<td>Ethylene</td>
<td>11.1 ppm</td>
<td>0.3 ppm</td>
</tr>
<tr>
<td>Propane</td>
<td>~ 0 ppm</td>
<td>~ 0 ppm</td>
</tr>
<tr>
<td>VOC (M320)</td>
<td>10.5 ± 2 ppm (C3)</td>
<td>0.3 ± 2 ppm (C3)</td>
</tr>
<tr>
<td>VOC (M25A - M320)</td>
<td>2.6 ± 11 ppm (C3)</td>
<td>0.8 ± 12 ppm (C3)</td>
</tr>
</tbody>
</table>

*Typical State VOC Permit Limits range from 10 – 75 ppm (C3)*
FTIR Surrogates
Comparison with and without the use of surrogates

- Synthetic Spectra
- Mixture of propane, butane, pentane, hexane
- Typical relative concentrations in NG gas
- Only propane and butane used in analysis model

<table>
<thead>
<tr>
<th>Nominal Total Alkanes</th>
<th>Measured Total Alkanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 ppm (C3)</td>
<td>21.6 ppm (C3)</td>
</tr>
<tr>
<td>17 ppm (C3)</td>
<td>19.2 ppm (C3)</td>
</tr>
<tr>
<td>11.7 ppm (C3)</td>
<td>12.6 ppm (C3)</td>
</tr>
</tbody>
</table>

Low error on Alkanes total contribution
Speciated Method Using FTIR

- Produces more accurate NMHC and VOC values compared to the Difference method.
- Speciated Method has much lower overall error in the analysis.
  - The Relative Error of the Speciated Method was ~12% compared to >143% for the Direct FID Method example here.
  - Even if you were off by 50% of the concentration of higher HCs using a surrogate for C4 and above you would still have a NMHC (or VOC) value that is more representative of what is present with a much lower overall error.
  - The Spectra are all saved and they can be validate post test.
- There are many published comparisons showing the validity of using FTIR for NMHC and VOC analysis as compared to the FID-based Methods.
Summary

- The Problem is not with FID Analyzers that are used for NMHC or VOC but with the Difference Method itself.
  - The FTIR THC and CH4 values have been shown to be well within 10% of the FID–based values
  - There is an inherent error in the Difference method that propagates exponentially and when CH4 (and/or Ethane) ≥ ~50% of the THC concentration
  - You must use another method such as Speciated Methods like FTIR or GC for CNG type fueled engine emissions for accurate VOCs

- For Quad J and Quad Z the only way to get closer to the true value with overall lower uncertainty for NMHC and VOC values is by using a speciated method.

- MKS Offers Free Training on FTIR to Regulators
  - April 2016 ASTM D6348 Hands On Method Training at MKS Office in Austin, TX
  - 2015 presented two webinars on how to validate MKS FTIR data in the field and a review of FTIR in general. Presentations available upon request.
  - Willing to host more hands on training and webinars – just say the word.
Sample of References on FTIR vs FID Study Comparisons


