Engine Testing with Portable Analyzers

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Outline of presentation

• Review two recent white papers on performance of portable electrochemical based analyzers
• Instrumentation limitations & sensor technology
• Reasons and solution to eliminate measurement variability
  • Temperature, pressure, cross sensitivity, etc.
• Sample transport and handling
• Test protocols and reporting
Title - Exhaust NO/NOx Ratio from Lean Burn Natural Gas Engines

Daniel B. Olsen and Morgan Kohls - Engines and Energy Conversion Laboratory, Colorado State University
Gregg Arney - Southern California Gas Company (So Cal Gas)

NO2 to NO ratio can be significant with ultra lean conditions or when using oxidation catalyst.

Large NO2/NOx ratios may result in additional uncertainty in NOx Measurements since the most common technique "chemiluminescent" was developed for low NO2/NOx ratios.

Three measurement technologies were tested

• Chemiluminescent
• Electro-Chemical sensors
• Fourier Transform Infrared (FTIR) Spectroscopy
White paper conclusions

“The portable analyzer with chemical cell technology was found to be the most accurate for measuring exhaust NOx with Large NO2/NOx ratios.”

Some reason:

• Electrochemical sensors measure both NO and NO2 for a true NOx value.

• Chemiluminescent does not measure NO2. It converts NO to NO2 for measurement. NOx converters loose NO2 sample integrity.

• FTIR – Uncertainties due to interference with water. Water absorbs infra-red radiation in many of the same wavelength bands as NO2 and NO.
Electrochemical Sensor - Linearity Study

- Two manufacturers of portable analyzers participated in this study
- Each provided two analyzers where one was calibrated as the “protocol” and the other as the “alternative”. Total of 4 analyzers tested side by side.
- The “Protocol” method analyzers used calibration gases in the high, medium and low range as is required for EPA Method 7E testing
- The “Alternative” method analyzers used one medium range concentration.

<table>
<thead>
<tr>
<th>EPA Protocol Gas</th>
<th>&quot;Alternative&quot; medium range concentration</th>
<th>&quot;Protocol&quot; used high, medium and low range concentration (EPA method 7E)</th>
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</thead>
<tbody>
<tr>
<td>CO</td>
<td>100 ppm</td>
<td>890, 249, 150, 100, and 50 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>50 ppm</td>
<td>50, 25, 15, and 8.1 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>80 ppm</td>
<td>30 ppm</td>
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Source testing results - Concentration averages from runs after calibrating portable analyzers using the 3 “protocol” concentrations compared to one “alternative” concentration.

<table>
<thead>
<tr>
<th></th>
<th>Analyzer A</th>
<th>Analyzer B</th>
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<tr>
<td></td>
<td>CO</td>
<td>NO</td>
</tr>
<tr>
<td><strong>Boiler Setting 1</strong></td>
<td></td>
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<tr>
<td>Average Protocol</td>
<td>12.27</td>
<td>3.65</td>
</tr>
<tr>
<td>Average Alternate</td>
<td>11.98</td>
<td>4.12</td>
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<tr>
<td><strong>Boiler Setting 2</strong></td>
<td></td>
<td></td>
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<tr>
<td>Average Protocol</td>
<td>27.11</td>
<td>3.23</td>
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<tr>
<td>Average Alternate</td>
<td>27.07</td>
<td>3.49</td>
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<td><strong>Boiler Setting 3</strong></td>
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<td>Average Protocol</td>
<td>201.62</td>
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<td>Average Alternate</td>
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<td>4.01</td>
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<td><strong>Boiler Setting 4</strong></td>
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<td></td>
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<tr>
<td>Average Protocol</td>
<td>15.29</td>
<td>16.07</td>
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<tr>
<td>Average Alternate</td>
<td>15.44</td>
<td>15.73</td>
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</tbody>
</table>

* CO readings show excellent reproducibility, but apparently the calibration concentration was entered incorrectly within 1.25 ppm, within 1 ppm, within 3 ppm *, within 1 ppm.
Findings and recommendations

• Low level linearity proved accurate by meeting EPA Method 301 validation for NOx, NO, and CO.

• NO₂ cell performance is likely as good as NO and CO, this study simply did not include sources with significant levels of NO₂.

Additional note:

• Drop tubes could allow simplified testing on sources without NO₂; preliminary work presented in this paper could be used for further investigation.
Instrumentation - Nothing Measures Perfectly

All sensor technologies have measurement variability in uncontrolled base forms.

- Temperature Influences (drift)
- Cross-sensitivity (to other gases)
- Flow sensitivity – must be controlled
- Technology specific concerns:
  - O2 quenching & converter efficiency – Chemiluminescent
  - Vibration and pressure – optical bench like NDIR
  - Moisture – FTIR

Portable EC Emission Analyzers - no different

- User should know the technology used, and test within the limits
- Use procedures (test method) that eliminate the sources of variability
- Use an “Emission Grade Analyzer”
- Address the site or technical limitation prior to testing
Manufacturing solutions - Emission Grade Analyzer design and manufacturing innovation help to eliminate measurement variability

Portable Analyzer for Combustion Emissions (PACE-1 2007) Specifies analyzer requirements.
Emission Grade Portable Analyzers – Reasons for use

- **Accuracy** - 3rd party verified (EPAs, associations, etc)
- **Technology advancements**
  - Continuous temp compensation
  - Better thermal stability
- **Intuitive interfaces**
  - Wireless connectivity
- **Many data acquisition options**

**Complete multi-gas systems $8-14K**
What is an Electrochemical Sensor?

- Similar to car battery
- Dissimilar metals (Cathode & Anode)
- Electrolyte matrix

- Gas enters through diffusion barrier
- Chemical Reaction (i.e. oxidation) Ion Exchange
- Each sensor is gas specific (through sensor chemistry and interference gas filtration)
- Electric current generated is proportional to gas concentration permeating through diffusion barrier
Example of installed sensors and gas path

CO gas path is separate due to:
• Concentration
• Cross sensitivity

EC analyzer provide a continuous measurement
Displays shows concentration as low as 1/sec

Sample comes in dry from on-board Peltier Chiller
Pressure can influence EC sensor output. Ambient conditions are required for proper diffusion into sensor. Extreme high, or low pressures or sample flow rate can change diffusion rate and output.

*How can this happen?* Field conditions that change pressure (low or high)

- Calibration - equipment or procedures used
- Source – Probe Location
- Analyzer – Sample pump degradation
Emission Grade Analyzers - control flow rate through precision valves and/or orifice plates. Newer analyzers measure and display flow rate.

Use Proper Calibration Procedures and Equipment

• Calibrate with overflow to ambient, or
• Alternative – use “Flow Matching” regulator
• Record and monitor flow during calibration and make sure both match (within 10%)
• Dynamically control flow rate (variable speed pump or manual
Calibration Flow Device – this one uses orifice plate to ambient to minimize gas waste

Demand Flow Regulator
No excess gas
DO NOT USE - dual gages as primary control of calibration gas!

Hints - Tank Pressure > 300 psi.
NOTE - EC is linear technology - Test bottled gas with analyzer to assure concentration level & acceptance.
If sample port is at high pressure location (i.e. In manifold or before turbo charger) sample from by-pass device (i.e. "T")

**Method 1**

- $X_{DS} = 8$ Stack Diameters
- $X_{US} = 2$ Stack Diameters

**CTM-030**

- $X_{DS} = 5$ Stack Diameters
- $X_{US} = 3$ Stack Diameters
Saturation (or over-exposure) of sensor.

At extreme concentrations or long-term exposure, the sensor chemistry can be temporarily depleted. Not enough $O_2$ for oxidation process, not enough moisture for electrolyte.

*How can this happen?*

• Long term calibration – typical cal. gas contains no $O_2$, and no moisture.
• Tuning out-of-control high concentration sources or (pre-catalyst)
• Long term source testing *(Concentration dependent)*
• Results in reduce sensor life – Used up sensor.
The fresh air purge is the process where sensors “breath” to replenish and balance $O_2$ and moisture in the electrolyte solutions for saturation (overexposure).

Allow fresh air purging during tuning and between testing:

- Improves accuracy by eliminating drift
  - Extends sensor life
  - Purge time is concentration dependent and recommended by manufacturer

- Utilize dilution system, use Ambient $O_2$ as for dilution gas. Sensor exposure divided by dilution factor. Displays corrected concentrations.
Example - *Manufacturer recommended purge times*

<table>
<thead>
<tr>
<th>Measurement parameter</th>
<th>Concentration [ppm]</th>
<th>Test time [min]</th>
<th>Recommended rinse time [min]</th>
<th>Calibration cycle in months</th>
<th>Filter service life</th>
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</thead>
<tbody>
<tr>
<td>NO</td>
<td>50</td>
<td>90</td>
<td>5</td>
<td>3</td>
<td>approx. 120.000ppm h (filter exchangeable)</td>
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<tr>
<td></td>
<td>100</td>
<td>60</td>
<td>5</td>
<td>3</td>
<td>3</td>
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<td></td>
<td>200</td>
<td>30</td>
<td>5</td>
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<td>500</td>
<td>20</td>
<td>10</td>
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<td>1</td>
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<td>2000</td>
<td>10</td>
<td>20</td>
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<tr>
<td></td>
<td>3000</td>
<td>5</td>
<td>30</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>NO low</td>
<td>10</td>
<td>90</td>
<td>5</td>
<td>3</td>
<td>approx. 40.000ppmh</td>
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<td></td>
<td>20</td>
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<td>5</td>
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<td>10</td>
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</tr>
<tr>
<td></td>
<td>300</td>
<td>10</td>
<td>20</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
Most “emission grade” analyzers use a combination:

**Provide Thermal Stability through design -**

- Monitor sensor temperature and utilize continuous temperature compensation
  - 1000s of sensors, many years = well characterized
- Isolate & protect sensor from temp changes
  - “sensor chamber” from ambient condition
- Physically maintain thermal envelop by housing in truck
- Warm up analyzer for 20 min prior to testing.
Measurement Variability due to: *Cross Sensitivity*

Some EC sensor are cross sensitive to other gases in exhaust stream – Most notable is the CO sensor response to NO and H2.

**Solutions for cross sensitivity**

- Maintain Filters (scrubbers) - remove before depleted (i.e. NOx beads before the CO sensor)
  - **External filters** – replace beads when color changes
  - **Internal filters** – On sensor = per ppm hr. counter or per manufacturer

- Electronically cross compensate by measurement (next slide)
- Identify cross sensitivity through the calibration procedure.
Measurement Variability due to: *Cross Sensitivity*

<table>
<thead>
<tr>
<th>Target gas (Sensor)</th>
<th>CO</th>
<th>NO</th>
<th>SO₂</th>
<th>NO₂</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0</td>
<td>0</td>
<td>0 ₁³</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO(H₂)</td>
<td>---</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0</td>
</tr>
<tr>
<td>CO(H₂) low</td>
<td>---</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>---</td>
<td>0 ₁₀ (w) ₁¹</td>
<td>6% ₁²</td>
<td>0</td>
</tr>
<tr>
<td>NO low</td>
<td>0</td>
<td>---</td>
<td>0 ₁₀</td>
<td>&lt;5% ₁²</td>
<td>0</td>
</tr>
<tr>
<td>NO₂</td>
<td>0</td>
<td>0</td>
<td>&lt;−2%</td>
<td>---</td>
<td>−20% ₁²</td>
</tr>
<tr>
<td>SO₂</td>
<td>&lt;5% ₁²</td>
<td>0</td>
<td>---</td>
<td>−110% ₁²</td>
<td>0 ₁₀</td>
</tr>
<tr>
<td>SO low</td>
<td>&lt;5% ₁²</td>
<td>0</td>
<td>---</td>
<td>−110% ₁²</td>
<td>0 ₁₀</td>
</tr>
<tr>
<td>CxHy</td>
<td>35% ₁⁰</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0 ₁₀</td>
<td>0</td>
</tr>
<tr>
<td>H₂S</td>
<td>&lt;2% ₁²</td>
<td>&lt;15% ₁²</td>
<td>&lt;20% ₁²</td>
<td>−20% ₁²</td>
<td>---</td>
</tr>
</tbody>
</table>

₁⁰ With non-saturated filter.
₁¹ w = Changeable filter
₁² Is compensated if analyzer contains/measures the cross-gas (NO plus NO₂)

Example: chart of cross sensitivity response
EC sensors use chemistry for operation. The chemistry simply wears out, but maintains linear response. No decrease in accuracy over time. They just get older.

**Solution for Aging Sensor**

- Talk Louder and repeat yourself
- Replace sensor
  - Plug & Play
  - New developments 3-year O2, 6-year other sensors
Testing Sample Handling and Transport

Engine Stacks
• Consistent shape – round
• Not – insulated
• Diameter 6' – 30"
• Usually no ladder or platform
• Hot – 900º F

• Important point – Sample handling equipment should not alter, contaminate or transform the sample in any way.
Sample probes and hoses

- Sample probes and hoses

  Probes and sample lines are non-reactive.

  stainless steel, Teflon®, or glass

  All fittings are non-reactive

  DO NOT USE - brass, rubber, Viton, or the hose from Pep Boys or Advanced Auto Parts with silicon and schedule 40 pvc....
Non-Heated Sample Lines (Teflon® or SS)
- Standard teflon lines – NO² scrubbing in lean burn applications
- High velocity sampling – Small diameter Teflon lines – small surface area and minimal contact time nearly eliminates NO2 scrubbing (1.6 seconds to transport sample through 7 foot line)

Heated Sample Lines (Teflon® or SS)
- Sample must remain above boiling point of water up to sample dryer –

EPA guidance - If proven concentration of NO₂ is less than 10% then it does not need to be measured.
Note: Rich burn engine have negligible NO₂ because little oxygen is in exhaust
Sample Conditioning

• Most permits require data on “Dry Basis”.
  
  Extractive sampling - Moisture is removed through sample conditioning system
  
  Moisture acts as a diluent - Moisture reduces measured readings

• Wet Basis
  
  - Typically In-Situ, or across stack -CEMS
  – More common in Europe

• Emission grade portable analyzers have on-board sample conditioning systems
  
  • Peltier chiller - typical - lowers sample gas temperatures to drop out moisture
### Wet vs. Dry Basis

<table>
<thead>
<tr>
<th></th>
<th>Wet Basis</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen</strong></td>
<td>2.20%</td>
<td>2.53%</td>
</tr>
<tr>
<td><strong>Carbon Dioxide</strong></td>
<td>13.20%</td>
<td>15.23%</td>
</tr>
<tr>
<td><strong>Nitrogen</strong></td>
<td>71.10%</td>
<td>82.05%</td>
</tr>
<tr>
<td><strong>Carbon Monoxide</strong></td>
<td>1.000%</td>
<td>1.115%</td>
</tr>
<tr>
<td><strong>Oxides of Nitrogen</strong></td>
<td>0.020%</td>
<td>0.023%</td>
</tr>
</tbody>
</table>

Both are acceptable – just different.
Drop Tube
GMRC white paper recommendation:

This is acceptable sample line because rich-burn engine have negligible NO2 to scrub out
BUT – problems with Drop Tube
High potential for water to collect in horizontal runs. High potential to saturate sensors and ruin your day or until sensor dries out.

Recommendations:
1. Blow out line before sampling.
2. Eliminate low spots
Other way to eliminate measurement variability

**Procedural solutions - Testing protocols**

- EPA Reference Method 7E (portable EC is allowed – being used)
- CTM - 030, ASTM D6522 (portable EC specific - reference level methods)
- CTM-034 (for periodic monitoring)
- State & Local protocols (periodic up to compliance level)

**Periodic Monitoring Recommendation**

- CA SCAQMD Periodic Monitoring Protocol
  - 1110.2 for engines & 1146 for boilers

http://www.aqmd.gov/comply/formsbyrule.htm
Software has come a long way

<table>
<thead>
<tr>
<th>Date / time</th>
<th>% O₂</th>
<th>ppm CO</th>
<th>ppm NO</th>
<th>ppm NO₂</th>
<th>ppm NOₓ</th>
</tr>
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<td>17.22</td>
<td>525</td>
<td>7</td>
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</table>
Software has come a long way.
Thank you for your attention.

For additional information

www.testo350.co

If interested in onsite training or demonstration contact:

Craig McKim
Testo, Inc. (800) 227-0729