A calibration system for low range GPT calibrations of high sensitivity NOx and NOy monitors.

National Air Monitoring Conference
Nashville, TN
November 2 - 5, 2009

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NCore Gas Calibration Needs

• NCore gas monitoring requirements include Ozone and trace level CO, SO$_2$ and NOy.

• The NCore Quality Assurance requirements include:
  - Multipoint calibrations – as needed to 6 months
  - Span and Precision checks – 24 hrs to 2 weeks
  - Converter Efficiency checks – 2 weeks to monthly
  - Low level detection tests - annually

• The NCore Technical Assistance Document (TAD) recommends automated audits and “on the fly” real-time level 1 data validation
NOy Calibration Requirements

- NOx&y analyzers are only able to detect NO. In order to know if the NOx&y and NO\textsubscript{2} data are valid, it is vitally important to know if & how well the converter is working.
- The NCore TAD recommends that Multipoint calibrations be performed for both NO and NO\textsubscript{2} at the same concentrations.
- Dilution of NO\textsubscript{2} is possible from gas cylinders but is not recommended due to the long stabilization period for each point as well as the instability of certified cylinder concentrations.
- Gas Phase Titration (GPT) is preferable because it produces reliable NO\textsubscript{2} concentrations without long stabilization periods.
GPT NO$_2$ Calibrations

- GPT calibrators use Mercury vapor lamps to produce ozone which reacts with cylinder NO to produce NO$_2$.
- The lamps are unstable and inconsistent at the levels needed to produce ozone for low level GPT calibrations.
- Simply increasing the flow rate or decreasing the reaction volume limits the calibrator’s dynamic range and may make the calibrator un-useable for higher level GPT calibrations.
- The limitations of the API Model 700E’s ozone generator sets the lower limit of its NO$_2$ output to 50 ppb.
API 700EU vs API 700E

- Internal Photometer with GPT to < 3 ppb NO₂
- Support for 2 Pollutant Flow controllers
- Supports External Valve Driver (automates site)

- Internal Photometer with GPT 30 - 50 ppb NO₂
- Support for 2 Pollutant Flow controllers
- Supports External Valve Driver (automates site)
The API Model 700EU

- A flow fraction controller is installed after the ozone generator to permit less than 100% of the generated ozone to react with NO.

- This allows the ozone generator to work within its stable region while providing needed low outputs of NO₂.
Typical GPT steps

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Values Obtained for Converter Efficiency Calculations (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPTPS</td>
<td>Optional step. Used to increase the accuracy of the O₃ concentration during GPT generation mode.</td>
<td></td>
</tr>
<tr>
<td>GPT</td>
<td>Produces NO₂ test gas using GPT with the ozone generator ON. The O₃ lamp drive value is used from the previous GPTPS.</td>
<td>[NO]rem, [NOx]rem</td>
</tr>
<tr>
<td>GPTZ</td>
<td>Delivers NO gas only for determining baseline (“orig”) NO and NOx values. Ozone generator is OFF.</td>
<td>[NO]orig, [NOx]orig</td>
</tr>
</tbody>
</table>

(1) 40 CFR part 50 Appendix F, "Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence)"
GPTPS Step

- GPTPS stands for “GPT Pre-Set”
- Optional step. Used just prior to GPT step to increase O₃ accuracy.
- User sets target NO and O₃ value identical to GPT.
- M700EU generates ozone and flows zero air in place of NO gas (no titration takes place.)
- M700EU uses internal photometer to “dial-in” O₃ concentration requested.
- Once concentration has stabilized, O₃ generator drive value is stored for the requested O₃ concentration point.
- The stored O₃ generator drive value is then used during subsequent GPT step.
GPT Step

- $O_3$ and NO are mixed at the specified concentrations.
- $O_3$ value should be no more than 80% of the NO value to ensure complete reaction of $O_3$.
- $O_3 + NO \rightarrow NO_2 + O_2$
- Stoichiometric ratio is 1:1 between $O_3$ and NO2.
- Resultant NO value is recorded as $[NO]_{rem}$, NOX value as $[NOx]_{rem}$
GPTZ Step

• Delivers NO gas only.
• Identical to GPT step except O₃ generator is OFF.
• Used for determining baseline ("orig") NO and NOx values.
• Resultant NO value is recorded as [NO]₉₀₉₀, NOx value as [NOx]₉₀₉₀
M700EU Performance

M700EU GPT 10 PPB NO, 5 PPB O3
(Data from M200EU S/N 122)

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M700EU Performance

M700EU GPT 5 PPB NO, 3 PPB C3
(Data from M200EU S/N 122)

Time

Conc (PPB)

0 1 2 3 4 5 6 7 8 9 10 11 12

5/13/2009
14:00 14:09 14:38 15:07 15:36
16:04 16:33 17:02 17:31

NOx
NO
CO

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Conclusions

- NCore calibrators must be able to deliver NO$_2$ at the same concentrations as NO.
- External valve drivers and advanced data acquisition systems permit automated audit sequences and automatic level 1 validation.
- The support for 2 pollutant flow controllers provides accuracy at the low levels needed for calibration levels at NCore clean (rural) sites and for low level detection tests.
- Accurate GPT convertor efficiency tests may reduce the need for additional convertor checks with diluted NPN/IPN.
End of Presentation
Typical Gas Standards

- NYSDEC Primary NO Cylinder (NIST)
  - 48.52 ± 0.32 ppm NOx
  - 48.52 ± 0.32 ppm NO
  - Balance Nitrogen
- The specifications permit > 1% NO₂
The Model 700EU GPT
The Model 700EU GPT

Included Photometer

GPT PRESET MODE (GPTPS)
The Model 700EU GPT

GPTZero MODE (GPTZ)

O3 OFF
The Model 700E GPT Option

Note: Minimum ozone output from the generator is 50 ppb.
M700EU Performance

M700EU GPT 5 PPB NO, 3 PPB O3
(Data from M200EU S/N 122)

Conc (ppb)

NOx
NO
NO2

Time

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