Getting to 0.3% difference:
Calibrating a multi-gas calibrator to generate calibration gas concentrations under 1 ppb accurately

2022 National Ambient Air Monitoring Conference

August 24, 2022
Pittsburgh, PA
Introduction & Philosophy

- What is measurement uncertainty and why do we care?
  - Guidance on Uncertainty Measurement defines as “parameter, associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the measurand”
- Why chase accuracy?
- Are we meeting requirements or satisfying our objectives?
## EPA Requirements

<table>
<thead>
<tr>
<th>1) Requirement (NO\textsubscript{2})</th>
<th>2) Frequency</th>
<th>3) Acceptance Criteria</th>
<th>Information /Action</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Verification/Calibration</strong></td>
<td>Upon receipt/adjustment/repair/installation/moving</td>
<td>Instrument residence time ( \leq 2 \text{ min Dynamic parameter} \geq 2.75 \text{ ppm-min} \ All points ( \leq 2.1 % ) or ( \leq 1.5 \text{ ppb difference of best-fit straight line whichever is greater and Slope} \leq 0.05 )</td>
<td>1) 40 CFR Part 50 App F \ 2 and 3) Recommendation Multi-point calibration (0 and 4 upscale points) Slope criteria is a recommendation</td>
</tr>
<tr>
<td></td>
<td>Every 182 day and 2/ calendar year if manual zero/span performed biweekly Every 365 day and 1/ calendar year if continuous zero/span performed daily</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gaseous Standards</strong></td>
<td>All gas cylinders</td>
<td>NIST Traceable (e.g., EPA Protocol Gas) 50-100 ppm of NO in Nitrogen with ( &lt; 1 \text{ ppm NO}_2 )</td>
<td>1) 40 CFR Part 50 App F Sec. 1.3.1 \ 2) NA Green Book \ 3) 40 CFR Part 50 App F Sec. 1.3.1. A technical memo may change the concentration requirement. Gas producer used must participate in EPA Ambient Air Protocol Gas Verification Program 40 CFR Part 58 App A Sec. 2.6.1</td>
</tr>
<tr>
<td><strong>Zero Air/ Zero Air Check</strong></td>
<td>Every 365 days and 1/ calendar year</td>
<td>Concentrations below LDL</td>
<td>1) 40 CFR Part 50 App F Sec. 1.3.2 2 and 3) Recommendation</td>
</tr>
<tr>
<td><strong>Gas Dilution Systems</strong></td>
<td>Every 365 days and 1/ calendar year or after failure of 1 point QC check or performance evaluation</td>
<td>Accuracy ( \leq 2.1 % )</td>
<td>1, 2 and 3) Recommendation based on SO2 requirement in 40 CFR Part 50 App A-1 Sec. 4.1.2</td>
</tr>
<tr>
<td><strong>Detection (FEM/FRMs)</strong> Noise and Lower Detectable Limits (LDL)</td>
<td>Every 365 days and 1/ calendar year</td>
<td>Noise ( \leq 0.005 \text{ ppm} )</td>
<td>1) 40 CFR Part 53.23 (b) (definition &amp; procedure) \ 2) Recommendation- info can be obtained from LDL \ 3) 40 CFR Part 53.20 Table B-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower detectable level ( \leq 0.01 \text{ ppm} )</td>
<td>1) 40 CFR Part 53.23 (c) (definition &amp; procedure) \ 2) Recommendation \ 3) 40 CFR Part 53.20 Table B-1</td>
</tr>
</tbody>
</table>

EPA Validation template requirements for operational criteria for NO\textsubscript{2} from EPA QA Handbook Vol II, Appendix D, revision #1 dated 3/17
Who cares about small numbers?
Who cares about small numbers?
Dynamic Dilution Gas Calibrator

• Teledyne API T700U with 3 Mass Flow Controllers (MFCs)
• Whichever calibrator you use, spec MFCs to hit concentration targets – determines gas cylinder concentrations that will work
• EPA Protocol gas concentration options determined by vendor
Multi-Gas Calibrator error

- Error can’t be avoided; no standard or system is perfect.
- Error on the multi-gas calibrator’s generated span gas comes from these sources:
  - Diluent MFC
  - Source gas MFC(s)
  - Ozone Photometer & Generator (during GPT)
  - Zero Air Generator or Diluent cylinder
  - Gas cylinder
MFC Calibration & Standards

• Simple conceptually: connect calibrator MFCs to flow standard, generate flow, compare MFC flow with standard

• Direct measurement standard options include:
  – Piston provers (Mesa Labs DryCal)
  – Mass Flow meters (many vendors)
  – Bubble meters
  – Laminar Flow Elements
  – Sonic nozzles
  – Pressure orifices
MFC Calibration & Standards

• Piston Prover:
  – Volumetric time-of-flight measurement – time for air flow to push piston to top of cell for optical measurement
  – Counts as primary flow standard
  – Expensive piston provers rated for 0.15%-0.25% difference accuracy – our selection
  – Can be very sensitive, flow cell can be contaminated if user is not careful
  – *Very* expensive (up to $20k for flow cell!) at low flow range
  – Dilution calibrator adjusts flow based on pressure feedback – flow output will not be fully stable.
MFC Calibration & Standards

• Mass flow meter:
  – Typically stable, compact, relatively inexpensive ($2,000 each)
  – Accuracy rating from vendor as high as 0.5% difference
  – Can be ordered as battery-powered for convenient field checks
  – Dilution calibrator will not encounter pressure feedback, and output will therefore be stable
MFC Calibration & Standards

• What to choose? Balance these factors:
  – Requirements
  – Budget – not just money, but time also
  – Your own preference for accuracy and/or methods
  – If attempting high accuracy and low cost, look into third party certification of mass flow meters
  – Out own experience suggests that mass flow meter factory calibration can very well outdo the rated specs sometimes
Set up for calibration

• If possible, communicate data out from calibrator and from flow standards
• Enables large quantity of data collection for measurement error calculations, or calibration graphs
• Understand what calibrator believes it is doing even when calibration screen may obscure it
• Occasional discrepancy between value set in flow table and indicated flow, necessitating need to enter a “wrong” value or value that is offset by a small amount.
Calibration in progress
Calibration In Progress
Calibration In Progress
Calibration in progress

• On TAPI T700U, 3 MFCs with 20 setpoints = 60 setpoints
• Flow setpoint may take 10-60 minutes to calibrate. Adjust values, wait for stabilization and averages, repeat until satisfied.
• Verify all points after adjustment
• We assume 3-day process just for MFC calibration
• Using high-accuracy standards and being patient, we attempt to calibrate each point to 0.1% difference
## Calibration Data

### Teledyne API T700U Serial # 495 Span MFC 1 Calibration

**Location:** DC-800-B

**Teledyne API T700U Serial #:** 495

**Span MFC:** 1

**Calibration Date:** 6/29/2022

**Component Calibrated:** Gas MFC 1

**Standard Cal Date:** 5/26/2022

**Metrologist:** KMM

**Flow Cell:** ML-800-10

**Flow Standard Serial #:** 160834

**Flow Standard:** DC-800-B

**Flow Cell Serial #:** 139802

**Calibrated Measurements**

### Initial Measurements

<table>
<thead>
<tr>
<th>Point</th>
<th>Initial MFC Drive Voltage (mV)</th>
<th>Initial Table Flow (Std mL/min)</th>
<th>Indicated Initial Flow (Std mL/min)</th>
<th>Measured Initial Flow (Std mL/min)</th>
<th>Corrected Table Flow (Std mL/min)</th>
<th>Corrected Initial Flow (mV)</th>
<th>Measured Initial Flow (Std mL/min)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>250.0</td>
<td>10.6</td>
<td>10.6</td>
<td>10.3</td>
<td>10.3</td>
<td>10.2</td>
<td>10.2</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>500.0</td>
<td>21.7</td>
<td>21.7</td>
<td>21.2</td>
<td>21.2</td>
<td>21.2</td>
<td>21.2</td>
<td>0.0071</td>
</tr>
<tr>
<td>4</td>
<td>750.0</td>
<td>32.9</td>
<td>32.9</td>
<td>32.3</td>
<td>32.3</td>
<td>32.2</td>
<td>32.2</td>
<td>0.0310</td>
</tr>
<tr>
<td>5</td>
<td>1,000.0</td>
<td>43.8</td>
<td>43.7</td>
<td>43.0</td>
<td>43.0</td>
<td>42.9</td>
<td>42.9</td>
<td>0.0000</td>
</tr>
<tr>
<td>6</td>
<td>1,250.0</td>
<td>54.7</td>
<td>54.7</td>
<td>53.8</td>
<td>53.8</td>
<td>53.6</td>
<td>53.6</td>
<td>-0.0186</td>
</tr>
<tr>
<td>7</td>
<td>1,500.0</td>
<td>65.5</td>
<td>65.5</td>
<td>64.6</td>
<td>64.6</td>
<td>64.5</td>
<td>64.5</td>
<td>-0.0197</td>
</tr>
<tr>
<td>8</td>
<td>1,750.0</td>
<td>76.3</td>
<td>76.3</td>
<td>75.3</td>
<td>75.3</td>
<td>75.3</td>
<td>75.3</td>
<td>-0.0133</td>
</tr>
<tr>
<td>9</td>
<td>2,000.0</td>
<td>87.0</td>
<td>87.0</td>
<td>86.0</td>
<td>86.0</td>
<td>86.0</td>
<td>86.0</td>
<td>0.0098</td>
</tr>
<tr>
<td>10</td>
<td>2,250.0</td>
<td>97.7</td>
<td>97.8</td>
<td>96.6</td>
<td>96.6</td>
<td>96.6</td>
<td>96.6</td>
<td>0.0310</td>
</tr>
<tr>
<td>11</td>
<td>2,500.0</td>
<td>108.4</td>
<td>108.4</td>
<td>107.2</td>
<td>107.2</td>
<td>107.2</td>
<td>107.2</td>
<td>0.0073</td>
</tr>
<tr>
<td>12</td>
<td>2,750.0</td>
<td>119.0</td>
<td>119.0</td>
<td>117.7</td>
<td>117.7</td>
<td>117.7</td>
<td>117.7</td>
<td>0.0340</td>
</tr>
<tr>
<td>13</td>
<td>3,000.0</td>
<td>129.3</td>
<td>129.4</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>0.0000</td>
</tr>
<tr>
<td>14</td>
<td>3,250.0</td>
<td>139.8</td>
<td>140.0</td>
<td>138.6</td>
<td>138.6</td>
<td>138.6</td>
<td>138.6</td>
<td>0.0144</td>
</tr>
<tr>
<td>15</td>
<td>3,500.0</td>
<td>150.3</td>
<td>150.4</td>
<td>149.1</td>
<td>149.1</td>
<td>149.1</td>
<td>149.1</td>
<td>0.0000</td>
</tr>
<tr>
<td>16</td>
<td>3,750.0</td>
<td>160.1</td>
<td>160.8</td>
<td>159.6</td>
<td>159.6</td>
<td>159.6</td>
<td>159.6</td>
<td>0.0027</td>
</tr>
<tr>
<td>17</td>
<td>4,000.0</td>
<td>171.3</td>
<td>171.4</td>
<td>170.0</td>
<td>170.0</td>
<td>170.0</td>
<td>170.0</td>
<td>0.0029</td>
</tr>
<tr>
<td>18</td>
<td>4,250.0</td>
<td>181.7</td>
<td>181.7</td>
<td>180.3</td>
<td>180.3</td>
<td>180.3</td>
<td>180.3</td>
<td>0.0111</td>
</tr>
<tr>
<td>19</td>
<td>4,500.0</td>
<td>192.1</td>
<td>192.2</td>
<td>190.8</td>
<td>190.8</td>
<td>190.8</td>
<td>190.8</td>
<td>0.0081</td>
</tr>
<tr>
<td>20</td>
<td>4,750.0</td>
<td>202.7</td>
<td>202.8</td>
<td>201.2</td>
<td>201.2</td>
<td>201.2</td>
<td>201.2</td>
<td>0.0397</td>
</tr>
<tr>
<td>21</td>
<td>5,000.0</td>
<td>213.1</td>
<td>213.1</td>
<td>211.7</td>
<td>211.7</td>
<td>211.7</td>
<td>211.7</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Performance notes

• We’ve found that we can reliably output very low concentrations, though higher flows may be required to hit the target:
  – As low as 5 ppb NO2 via GPT
  – 20 ppb CO
  – 1 ppb SO2
What was all the effort for?

- Ambient low concentrations argue that span concentrations should match typical measurements
- For Oregon, this means CO < 500 ppb, SO$_2$ < 1 ppb, NO/NO$_2$/NO$_X$ < 5 ppb
- We’ve already asked EPA to allow lower span ranges in the validation template – 5 ppb is too high for us!
- MDL Testing – what can the analyzers actually measure accurately?
MDL Testing

• Teledyne API claims very low lower detection levels on U-series instruments – 20 ppb for CO, 50 ppt for SO2, NO2.
• We want to know the reality
• T500U and T200UP MDL testing we performed (EPA protocol cylinder) suggested MDLs of 0.279 and 0.183 ppb for NO2, respectively.
• Reasonably good performance! Definitely good enough to meet measurement objectives
• Could potentially measure better MDL performance with non-EPA protocol cylinders (lower ranges)
Conclusions

• Calibrating your calibrator’s MFCs to 0.3% difference is achievable!
• Worth your time? A decision every monitoring group will have to make
• We have enough reasons to chase accuracy, but your situation may not warrant it
Acknowledgements

- Thien Bui, EPA Region 7
- Francisco Silvas, CA ARB
- Michael Parker and Bryan Bibeau, Teledyne API
- William Cheung, formerly at Mesa Labs
Questions? Comments?

• Always feel free to reach out to me if you’d like to know more:

• matthew.shrensel@deq.oregon.gov