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

Matthew Shrensel | Oregon Department of Environmental Quality

Introduction & Philosophy

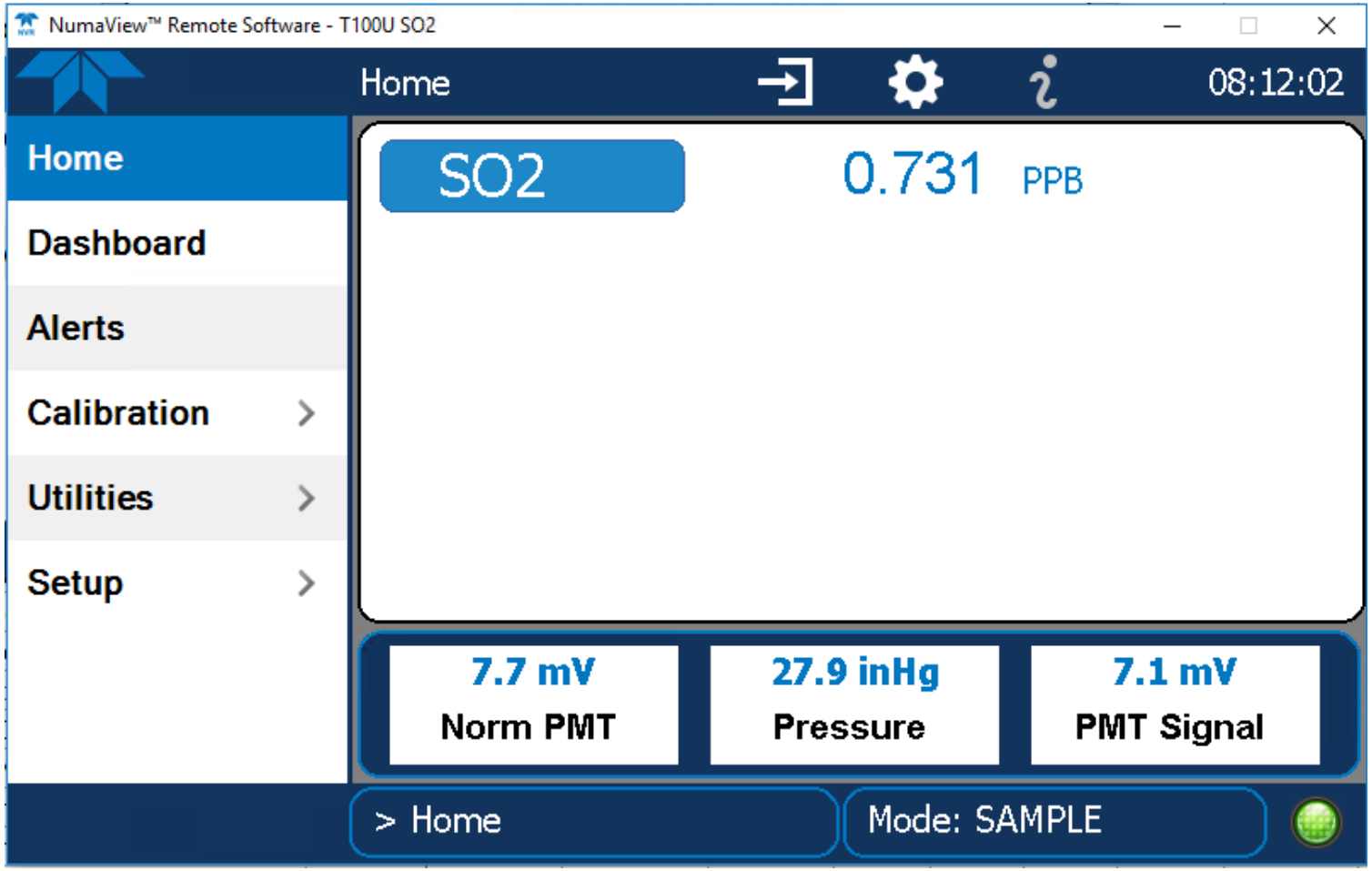
- What is measurement uncertainty and why do we care?
  - Guidance on Uncertainty Measurement defines as “parameter, associated with the result of a measurement, that characterizes the dispersion of values that could reasonably be attributed to the measurand”
- Why chase accuracy?
- Are we meeting requirements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

EPA Requirements

1) Requirement (NO_2)	2) Frequency	3) Acceptance Criteria	Information /Action
Verification/Calibration	Upon receipt/adjustment/repair/ installation/moving 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	Instrument residence time ≤ 2 min Dynamic parameter ≥ 2.75 ppm-min All points <± 2.1 % or ≤ ± 1.5 ppb difference of best-fit straight line whichever is greater and Slope 1 ± .05	1) 40 CFR Part 50 App F 2 and 3) Recommendation Multi-point calibration (0 and 4 upscale points) Slope criteria is a recommendation
Gaseous Standards	All gas cylinders	**NIST Traceable** (e.g., EPA Protocol Gas) 50-100 ppm of NO in Nitrogen with < 1 ppm NO_2	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 requirment. Gas producer used must participate in EPAAmbient Air Protocol Gas Verification Program 40 CFR Part 58 App A Sec. 2.6.1
Zero Air/ Zero Air Check	Every 365 days and 1/ calendar year	Concentrations below LDL	1) 40 CFR Part 50 App F Sec. 1.3.2 2 and 3) Recommendation
Gas Dilution Systems	Every 365 days and 1/ calendar year or after failure of 1 point QC check or performance evaluation	Accuracy < ± 2.1 %	1, 2 and 3) Recommendation based on SO2 requirement in 40 CFR Part 50 App A-1 Sec. 4.1.2
Detection (FEM/FRMs) Noise and Lower Detectable Limits (LDL) are part of the FEM/FRM requirements. It is recommended that monitoring organizations perform the LDL test to minimally confirm and establish the LDL of their monitor. Performing the LDL test will provide the noise information.			
Noise	Every 365 days and 1/ calendar year	***≤ 0.005 ppm***	1) 40 CFR Part 53.23 (b) (definition & procedure) 2) Recommendation- info can be obtained from LDL 3) 40 CFR Part 53.20 Table B-1
Lower detectable level	Every 365 days and 1/ calendar year	***≤ 0.01 ppm***	1) 40 CFR Part 53.23 (c) (definition & procedure) 2) Recommendation 3) 40 CFR Part 53.20 Table B-1

EPA Validation template requirements for operational criteria for NO2 from EPA QA Handbook Vol II, Appendix D, revision #1 dated 3/17

Who cares about small numbers?



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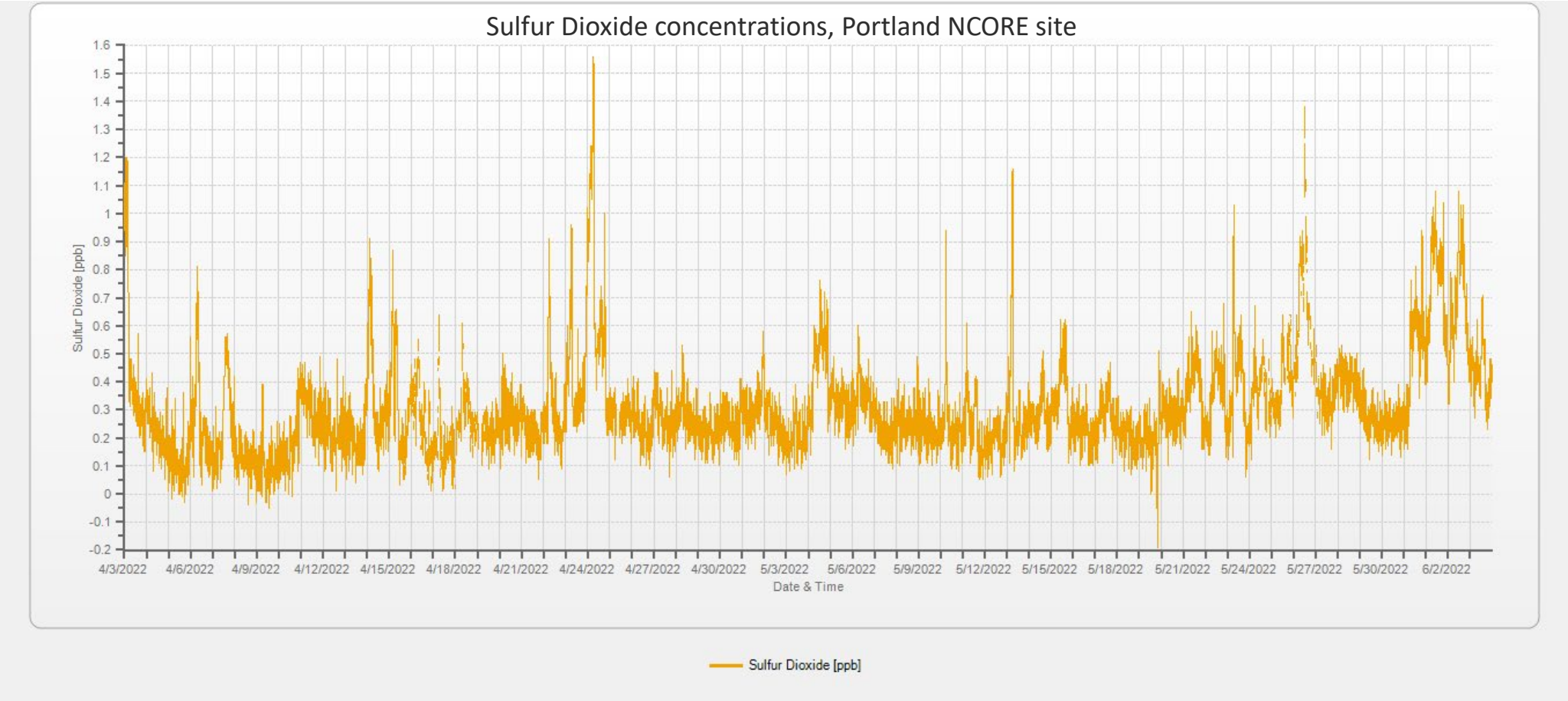
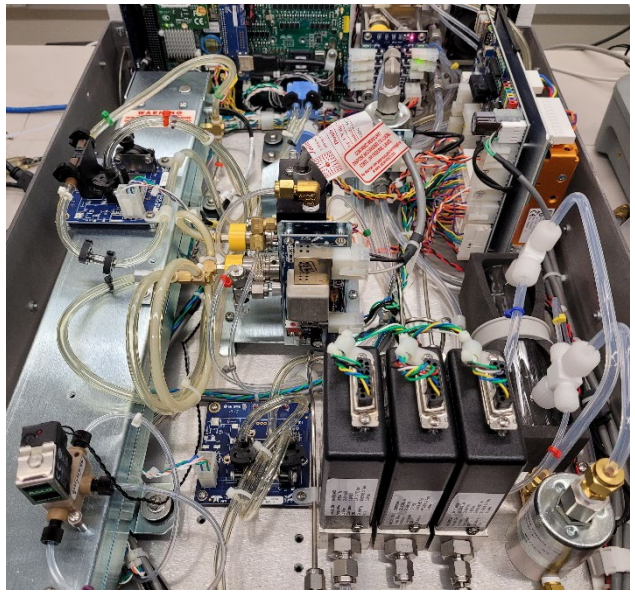


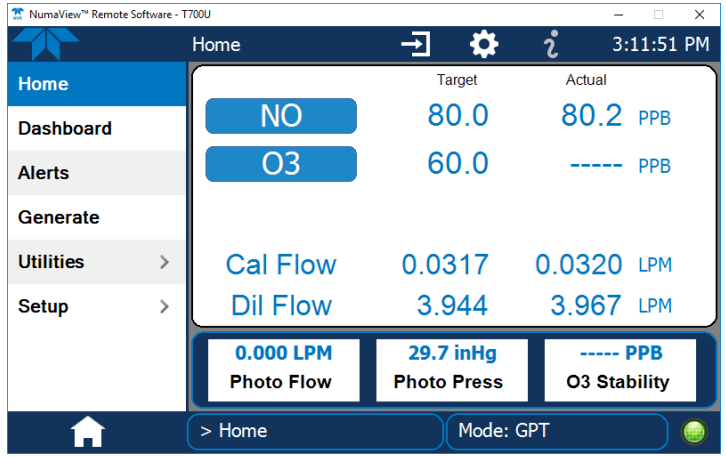
Dynamic Dilution Gas Calibrator

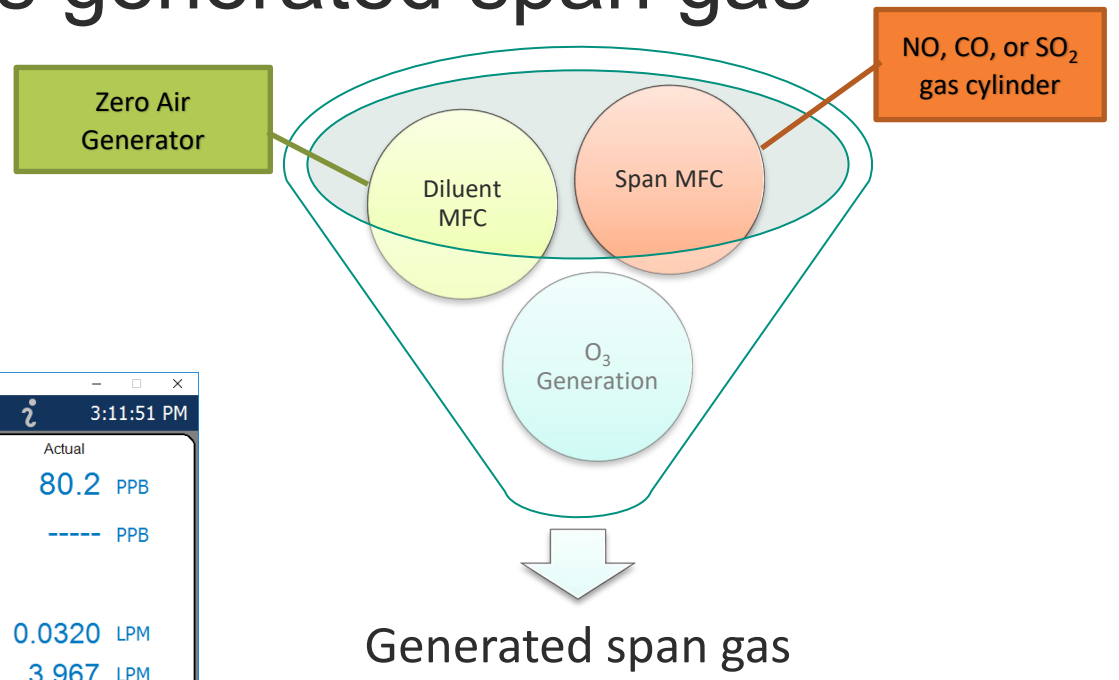
- Teledyne API T700U with 3 Mass Flow Controllers (MFCs)
- Whichever calibrator you use, spec MFCs to hit concentration targets – determines gas cylinder concentrations that will work
- EPA Protocol gas concentration options determined by vendor



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



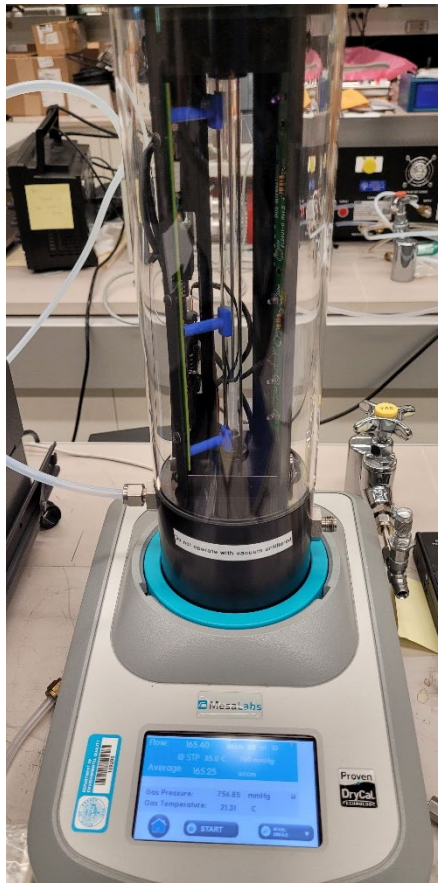


MFC Calibration & Standards

- 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

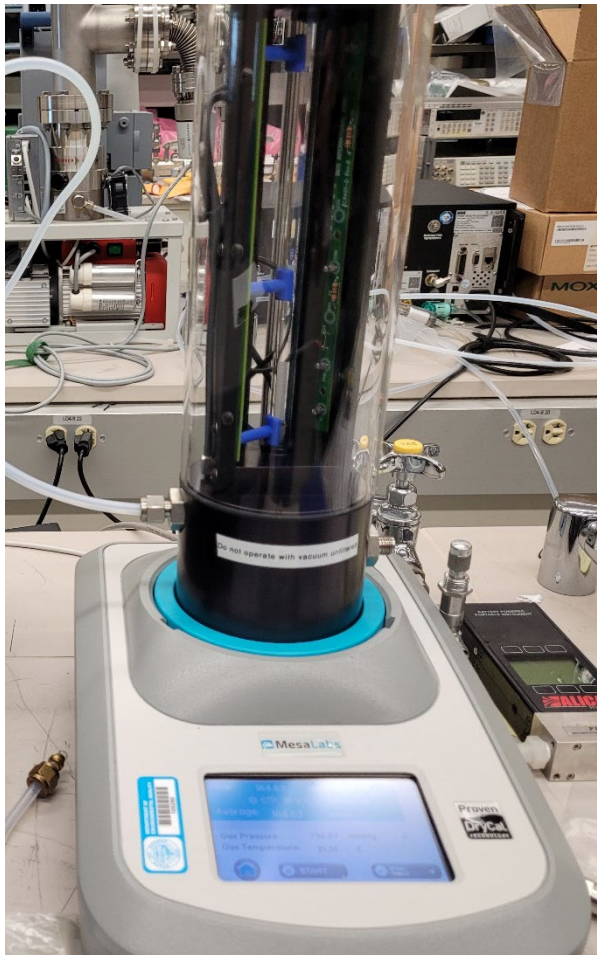
MFC Calibration & Standards

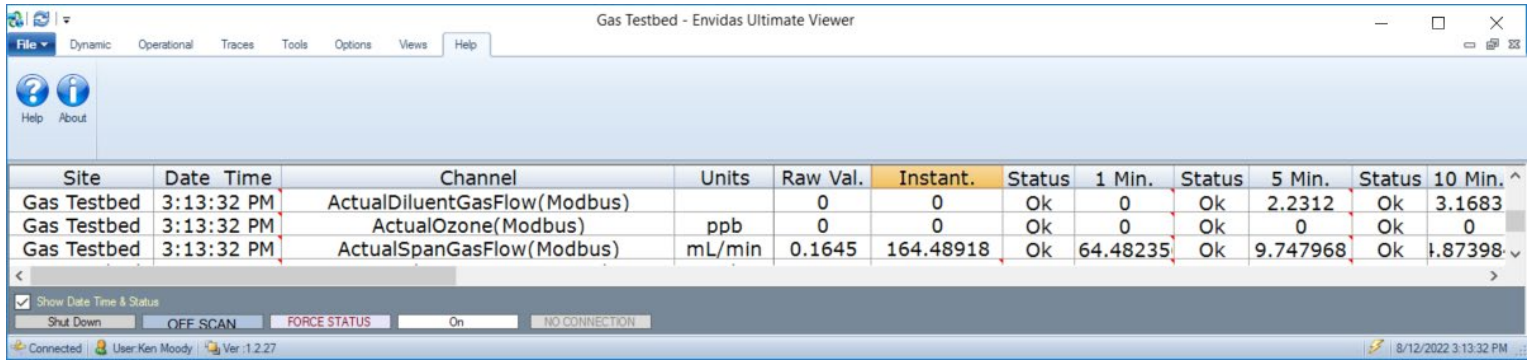
- What to choose? Balance these factors:
  - Requirements
  - Budget – not just money, but time also
  - Your own preference for accuracy and/or methods
  - If attempting high accuracy and low cost, look into third party certification of mass flow meters
  - Out own experience suggests that mass flow 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





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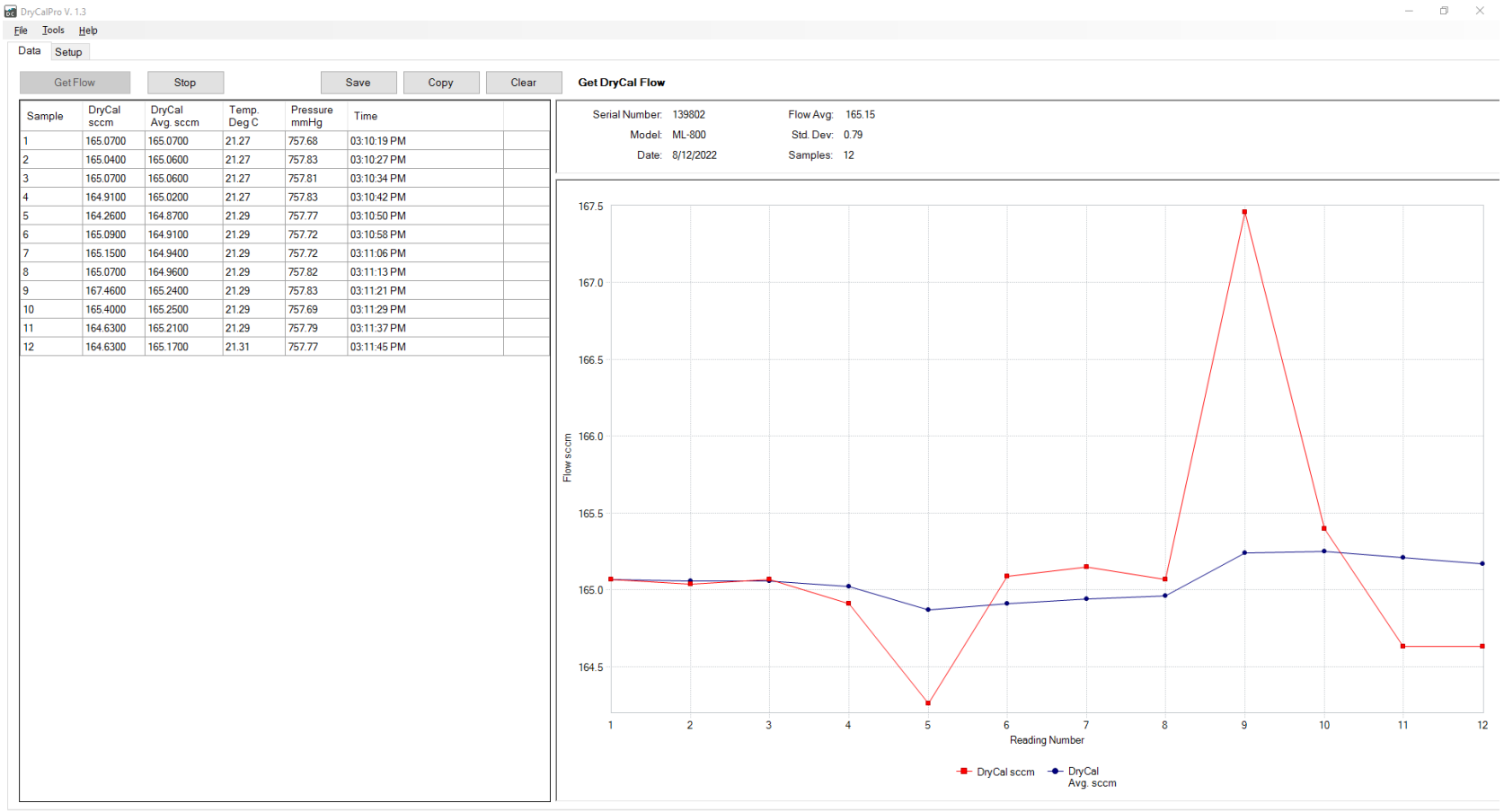
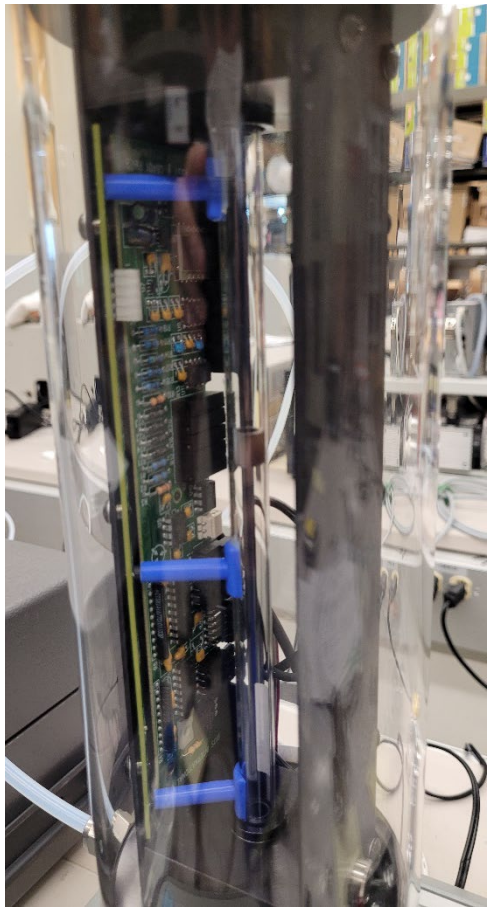


Sample	DryCal sccm	DryCal Avg. sccm	Temp. Deg C	Pressure mmHg	Time
1	165.0700	165.0700	21.27	757.68	03:10:19 PM
2	165.0400	165.0600	21.27	757.83	03:10:27 PM
3	165.0700	165.0600	21.27	757.81	03:10:34 PM
4	164.9100	165.0200	21.27	757.83	03:10:42 PM
5	164.2600	164.8700	21.29	757.77	03:10:50 PM
6	165.0900	164.9100	21.29	757.72	03:10:58 PM
7	165.1500	164.9400	21.29	757.72	03:11:06 PM
8	165.0700	164.9600	21.29	757.82	03:11:13 PM
9	167.4600	165.2400	21.29	757.83	03:11:21 PM
10	165.4000	165.2500	21.29	757.69	03:11:29 PM
11	164.6300	165.2100	21.29	757.79	03:11:37 PM
12	164.6300	165.1700	21.31	757.77	03:11:45 PM



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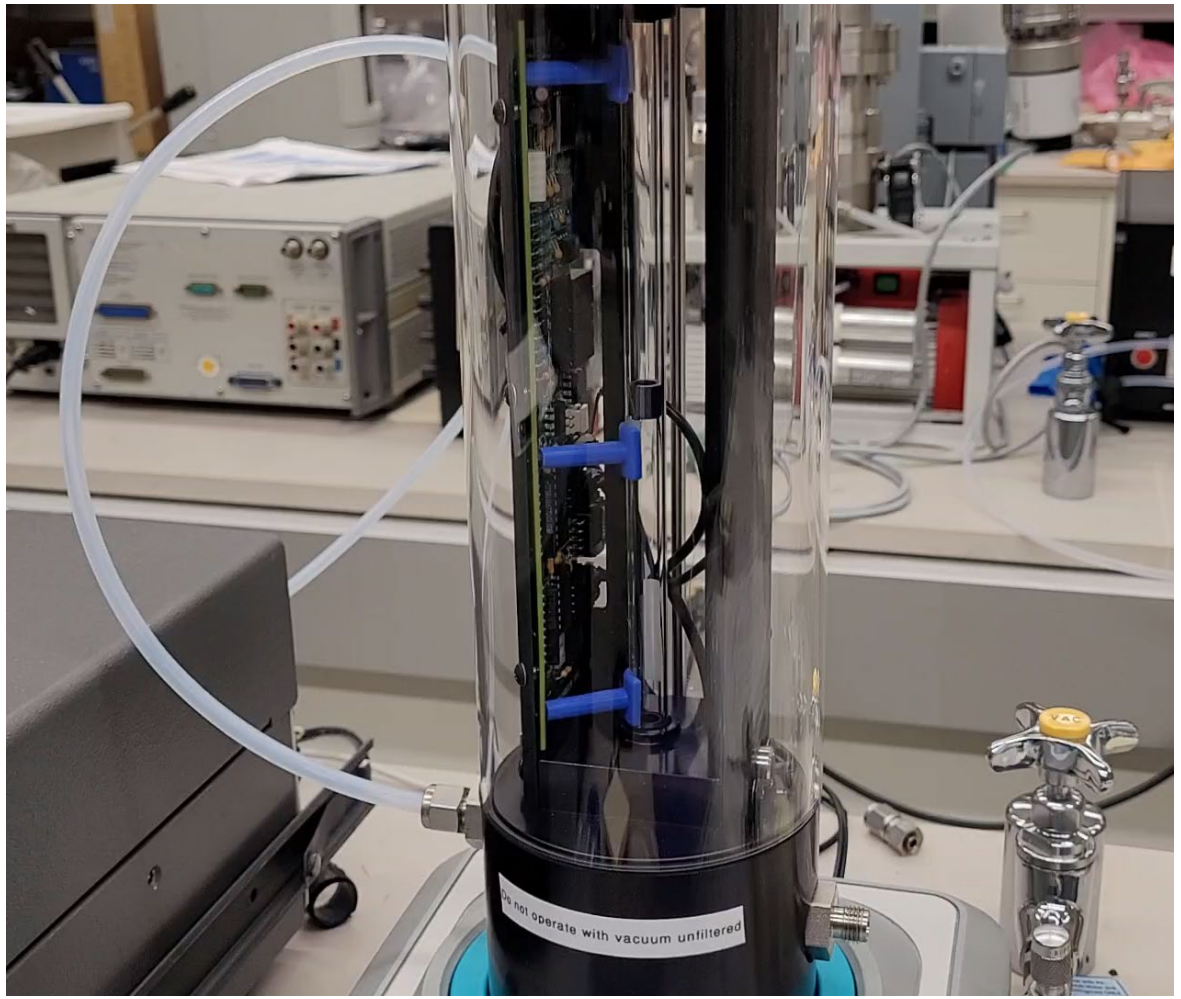

Calibration in progress

- 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

State of Oregon Department of Environmental Quality

Teledyne API T700U Serial # 495 Span MFC 1 Calibration

Location:	Lab	Flow Standard:		DC-800-B	Flow Standard Serial #:		160834
Metrologist:	KMM	Flow Cell:		ML-800-10	Flow Cell Serial #:		139802
Date:	6/29/2022	Component Calibrated:		Gas MFC 1	Standard Cal Date:		5/26/2022
MFC Slope:	1.000	Calculated Slope:	0.9996348	Correlation:	0.9999999	Likely % error:	0.07
MFC Offset:	0.0 mV	Calculated Offset:	0.0117819	Max % error:	0.0697837	Cal Expires:	6/29/2023

	Initial Measurements				Calibrated Measurements				
Point	Initial MFC Drive Voltage (mV)	Initial Table Flow (Std mL/min)	Indicated Initial Flow (Std mL/min)	Measured Initial Flow (Std mL/min)	Corrected Table Flow (Std mL/min)	Corrected Voltage (mV)	Indicated Flow (Std mL/min)	Measured Flow (Std mL/min)	% Difference
1	0.0	0.0	0.0	0.00	0.0	Uncorrected	0.0	0.00	N/A
2	250.0	10.6	10.6	10.32	10.3	Uncorrected	10.27	10.27	0.0000
3	500.0	21.7	21.7	21.32	21.2	Uncorrected	21.26	21.25	0.0471
4	750.0	32.9	32.9	32.30	32.3	Uncorrected	32.28	32.27	0.0310
5	1,000.0	43.8	43.7	43.00	43.0	Uncorrected	42.98	42.98	0.0000
6	1,250.0	54.7	54.7	53.84	53.8	Uncorrected	53.80	53.81	-0.0186
7	1,500.0	65.5	65.5	64.55	64.6	Uncorrected	64.55	64.59	-0.0619
8	1,750.0	76.3	76.3	75.34	75.3	Uncorrected	75.33	75.34	-0.0133
9	2,000.0	87.0	87.0	86.00	86.0	Uncorrected	86.04	85.98	0.0698
10	2,250.0	97.7	97.8	96.65	96.6	Uncorrected	96.66	96.63	0.0310
11	2,500.0	108.4	108.4	107.20	107.2	Uncorrected	107.25	107.21	0.0373
12	2,750.0	119.0	119.0	117.68	117.7	Uncorrected	117.73	117.69	0.0340
13	3,000.0	129.3	129.4	128.19	128.2	Uncorrected	128.14	128.14	0.0000
14	3,250.0	139.8	140.0	138.60	138.6	Uncorrected	138.73	138.71	0.0144
15	3,500.0	150.3	150.4	149.14	149.1	Uncorrected	149.19	149.19	0.0000
16	3,750.0	160.7	160.8	159.57	159.6	Uncorrected	159.70	159.60	0.0627
17	4,000.0	171.3	171.4	170.00	170.0	Uncorrected	170.10	170.01	0.0529
18	4,250.0	181.7	181.7	180.33	180.3	Uncorrected	180.38	180.36	0.0111
19	4,500.0	192.1	192.2	190.83	190.8	Uncorrected	190.94	190.81	0.0681
20	4,750.0	202.7	202.8	201.25	201.2	Uncorrected	201.38	201.30	0.0397
21	5,000.0	213.1	213.1	211.70	211.7	Uncorrected	211.70	211.70	0.0000

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