

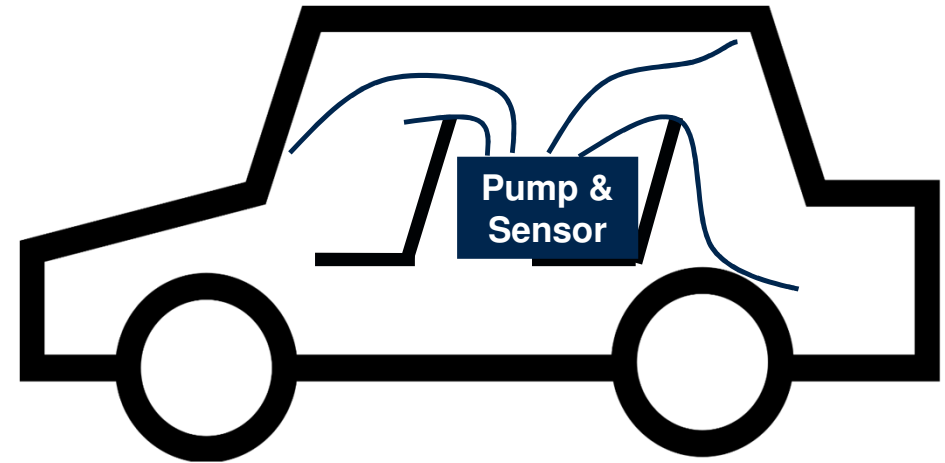


CO Sensor Response Study NO & NOx Analyzer Validation

June 6, 2018

HOW TO MEASURE MULTIPLE ZONES

- Sensor Options Available
 - Passive sensors
 - Small and easy to use
 - Rely on diffusion to reach sensor
 - Vacuum source sensors
 - Highest accuracy
 - Capable of multiplexing
- Measurement of driver breath level is required
 - Measuring levels throughout vehicle - FOR DEVELOPMENT ONLY
 - Assist in discovering source with multiplexing



Both Options Are Capable Of Accurate Measurements
Multiplexing System Under Development

CONVERSION FROM MASS/VOLUME TO PARTS/VOLUME

The molar volume of an ideal gas at 1 atmosphere of pressure:

22.414 L/mol at 0 °C,
24.465 L/mol at 25 °C.

The molar volume of an ideal gas at 100 kPa (average Detroit, Michigan, USA ground level air pressure)

22.710 L/mol at 0 °C,
24.789 L/mol at 25 °C.

Russian National Standard GOST R 33554-2015 Limits

	Concentration ppb (mol/mol)	Concentration ppm (mol/mol)	Concentration [$\mu\text{g}/\text{m}^3$]	Concentration [mg/m^3]	Molecular Weight g/mol	Gas Molar Volume L/mol
Formaldehyde (HCHO)	41	0.041	50	0.05	30.03	24.79
Nitrogen Dioxide (NO ₂)	108	0.108	200	0.2	46.01	24.79
Nitric Oxide [NO]	331	0.331	400	0.4	30.01	24.79
Carbon Monoxide [CO]	4425	4.425	5000	5.0	28.01	24.79
Methane [CH ₄]	77275	77.275	50000	50.0	16.04	24.79

Calibration Standards Are Typically Blended By Concentration



SENSORS CONSIDERED

ToxiRAE Pro II



- Honeywell Company
- Electrochemical sensor
- Wireless
- Diffusion sampling
- 30+ hours of operation
- 1 Hz Logging capable
- 0-500 ppm range
- 1 ppm resolution

Horiba VA-5111

- NDIR Detector
- Vacuum sampling (up to 1.0 L/min)
- Computer controlled (TCP/IP)
- Logging speed variable
- 0-50 ppm and 0-500 ppm ranges
- 0.001 ppm resolution (displays 0.01)



Comparison Of Passive And Active Detectors

TEST PLAN

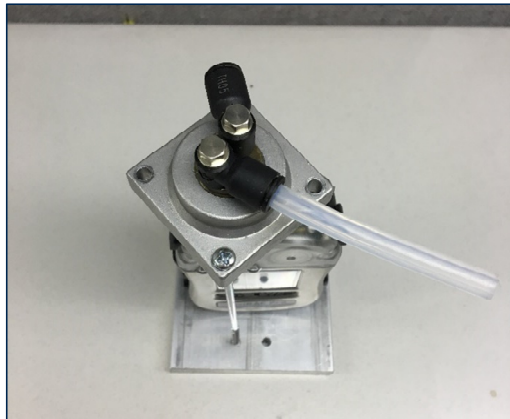
- Observe sensor response for 10, 20, and 30 second events
 - Solenoid switching ($\ll 1.0$ second) between CO bottle and zero air bottle
- Test gas of 50 ppm CO in balance N₂ (actual NIST Bottle Label = 50.74 ppm)
- Two flow rates of 0.5 and 1.0 L/min were tested
- ToxiRAE: Response differences with and without filter

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
CO_1 Sensor_1	50	Horiba VA-5111	CO_1	1 Hz	0.5	N	
CO_1 Sensor_2	50	Horiba VA-5111	CO_1	1 Hz	1	N	
CO_1 Sensor_3	50	Horiba VA-5111	CO_1	1 Hz	0.5	Y	
CO_2 Sensor_1	50	Horiba VA-5111	CO_2	1 Hz	0.5	N	
CO_2 Sensor_2	50	Horiba VA-5111	CO_2	1 Hz	1	N	
CO_2 Sensor_3	50	Horiba VA-5111	CO_2	1 Hz	0.5	Y	
ToxiRAE CO_1	50	ToxiRAE Pro II	CO	1 Hz	0.5		Y
ToxiRAE CO_2	50	ToxiRAE Pro II	CO	1 Hz	1		Y
ToxiRAE CO_3	50	ToxiRAE Pro II	CO	1 Hz	0.5		N
ToxiRAE CO_4	50	ToxiRAE Pro II	CO	1 Hz	1		N



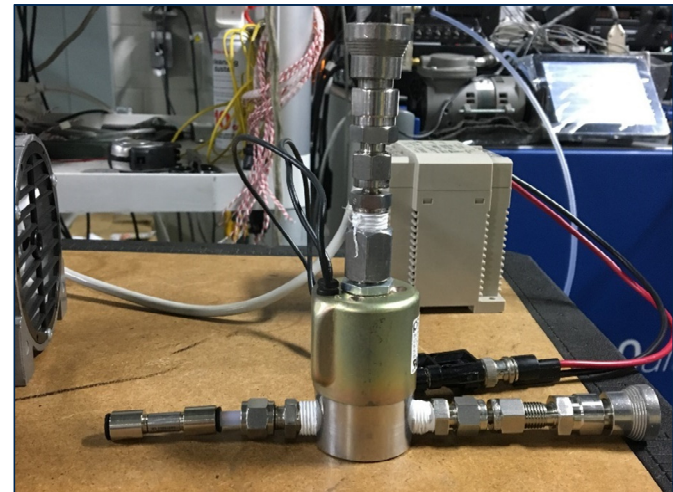
TEST PLAN

ToxiRAE Inlet System



Solenoid Valve

CO



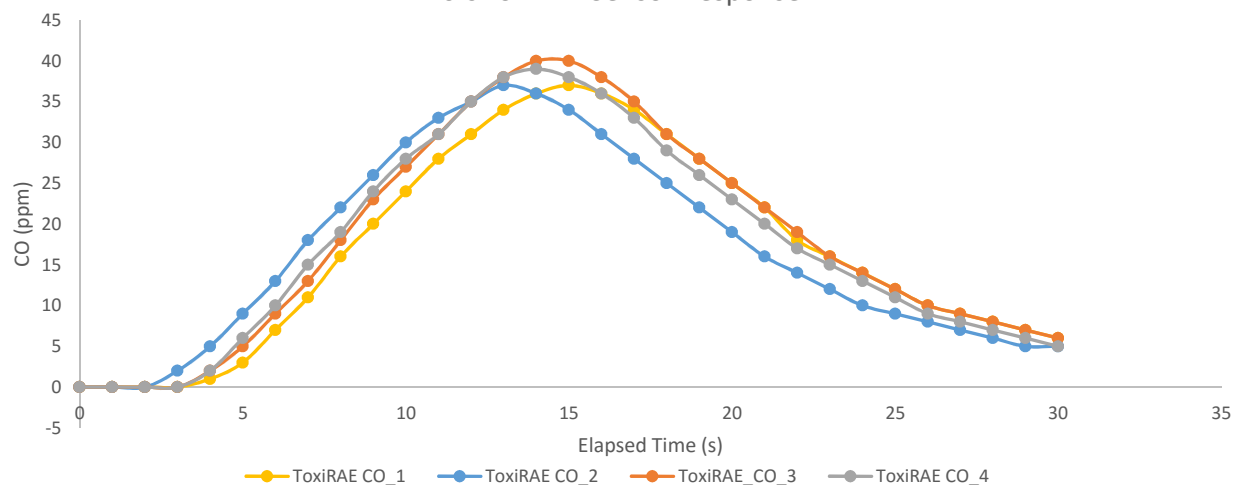
Zero
Air

Critical
Flow
Orifice

TOXIRAE 10 SECOND EVENT

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
ToxiRAE CO_1	50	ToxiRAE Pro II	CO	1 Hz	0.5		Y
ToxiRAE CO_2	50	ToxiRAE Pro II	CO	1 Hz	1		Y
ToxiRAE_CO_3	50	ToxiRAE Pro II	CO	1 Hz	0.5		N
ToxiRAE CO_4	50	ToxiRAE Pro II	CO	1 Hz	1		N

10-s ToxiRAE Sensor Response

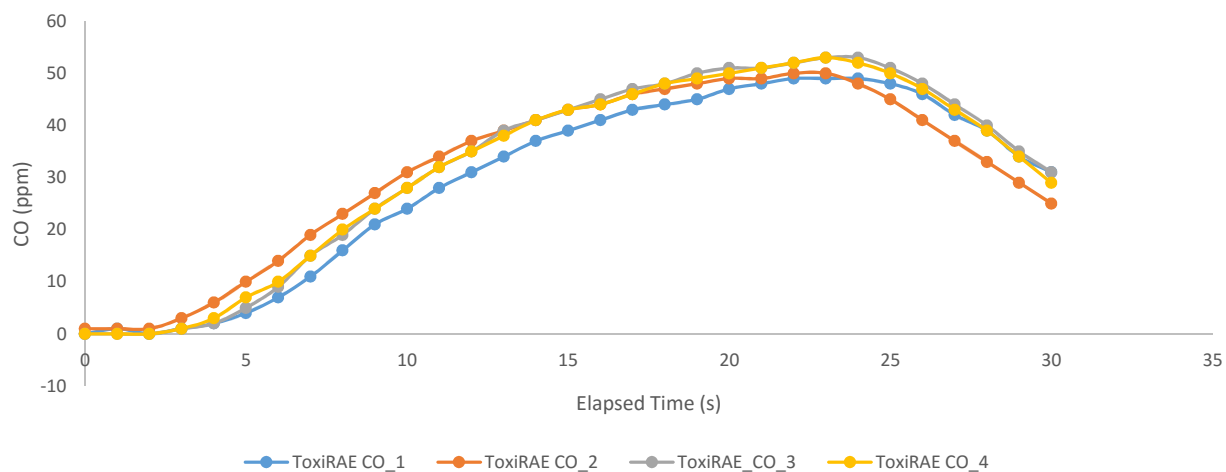


No Filter Lead To Higher Response In Same Time Period

TOXIRAE 20 SECOND EVENT

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
ToxiRAE CO_1	50	ToxiRAE Pro II	CO	1 Hz	0.5		Y
ToxiRAE CO_2	50	ToxiRAE Pro II	CO	1 Hz	1		Y
ToxiRAE_CO_3	50	ToxiRAE Pro II	CO	1 Hz	0.5		N
ToxiRAE CO_4	50	ToxiRAE Pro II	CO	1 Hz	1		N

20-s ToxiRAE Sensor Response

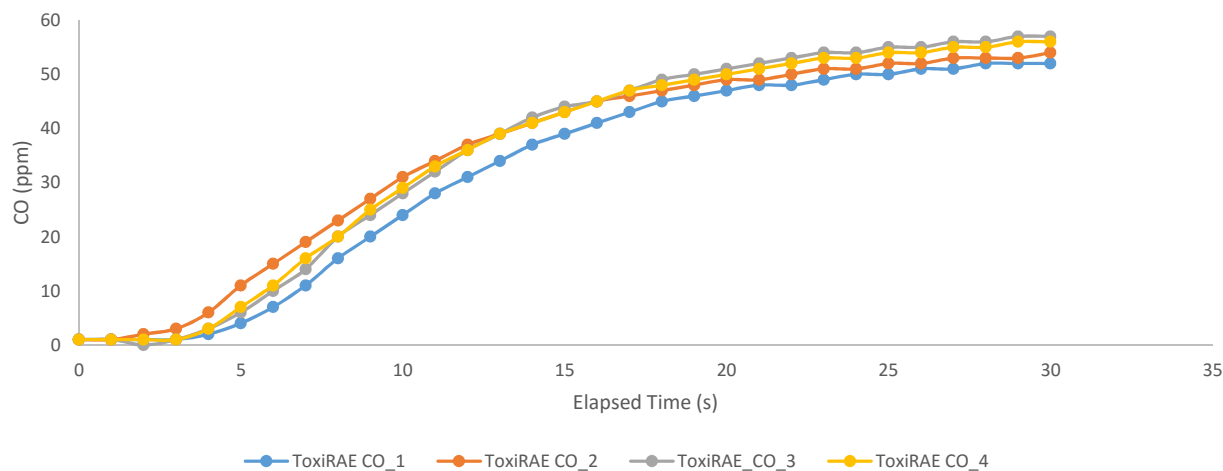


Similar Response; No Filter Read High (53 ppm)

TOXIRAE 30 SECOND EVENT

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
ToxiRAE CO_1	50	ToxiRAE Pro II	CO	1 Hz	0.5		Y
ToxiRAE CO_2	50	ToxiRAE Pro II	CO	1 Hz	1		Y
ToxiRAE_CO_3	50	ToxiRAE Pro II	CO	1 Hz	0.5		N
ToxiRAE CO_4	50	ToxiRAE Pro II	CO	1 Hz	1		N

30-s ToxiRAE Sensor Response

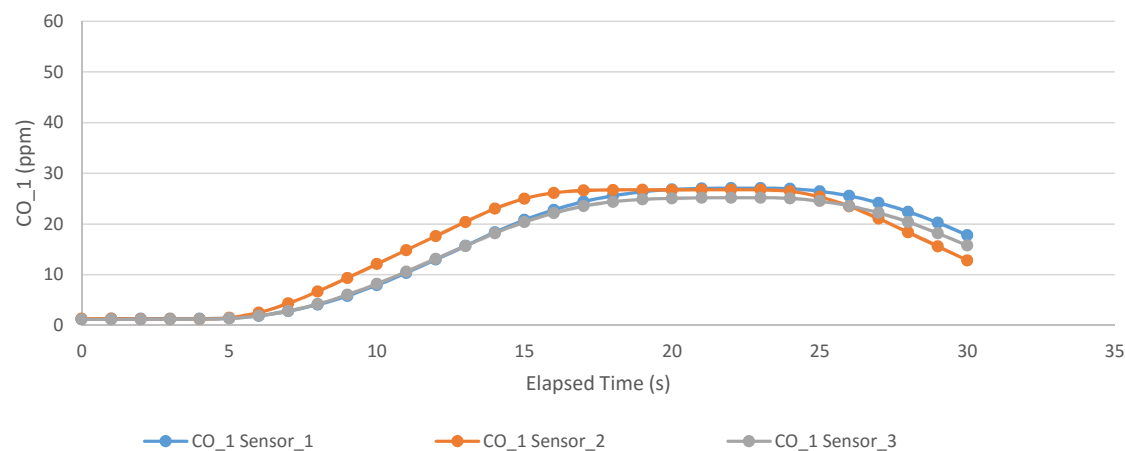


Similar Response; Filter Determined Peak Reading (Y: 54, N: 57)

HORIBA 10 SECOND EVENT (Analyzer 1)

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
CO_1 Sensor_1	50	Horiba VA-5111	CO_1	1 Hz	0.5	N	
CO_1 Sensor_2	50	Horiba VA-5111	CO_1	1 Hz	1	N	
CO_1 Sensor_3	50	Horiba VA-5111	CO_1	1 Hz	0.5	Y	

10-s Horiba VA-5111

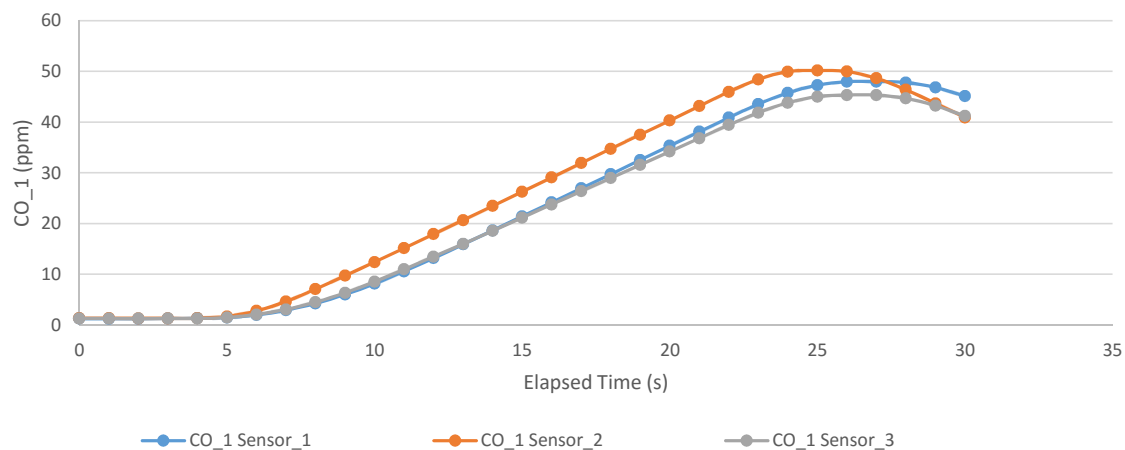


Similar Peak Reading; 1.0 L/min Slightly Faster Response

HORIBA 20 SECOND EVENT (Analyzer 1)

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
CO_1 Sensor_1	50	Horiba VA-5111	CO_1	1 Hz	0.5	N	
CO_1 Sensor_2	50	Horiba VA-5111	CO_1	1 Hz	1	N	
CO_1 Sensor_3	50	Horiba VA-5111	CO_1	1 Hz	0.5	Y	

20-s Horiba VA-5111

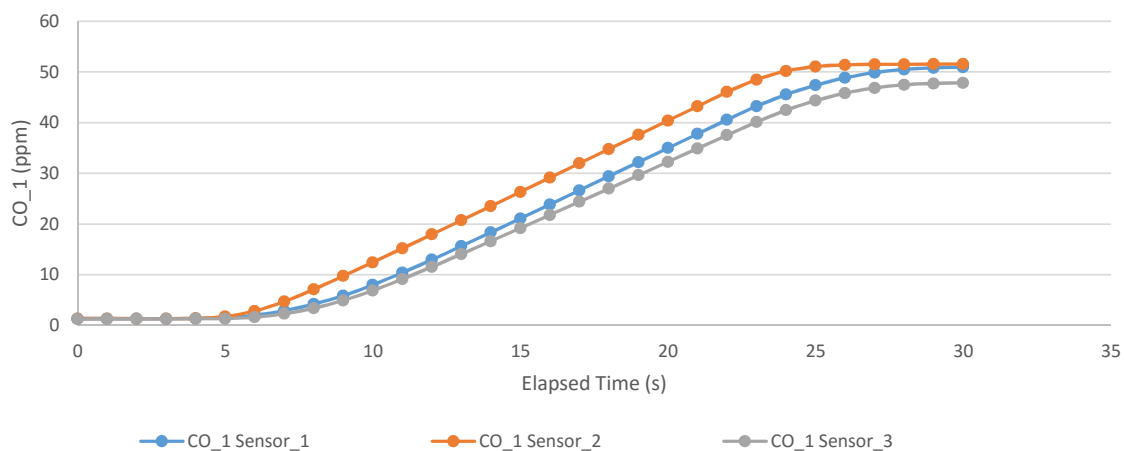


Vacuum Read Low (45 ppm); 1.0 L/min Slightly Faster Response

HORIBA 30 SECOND EVENT (Analyzer 1)

Test	Bottle (ppm)	System	Analyzer	Scan Rate	Flow Rate (L/min)	Vacuum (Y/N)	Filter (Y/N)
CO_1 Sensor_1	50	Horiba VA-5111	CO_1	1 Hz	0.5	N	
CO_1 Sensor_2	50	Horiba VA-5111	CO_1	1 Hz	1	N	
CO_1 Sensor_3	50	Horiba VA-5111	CO_1	1 Hz	0.5	Y	

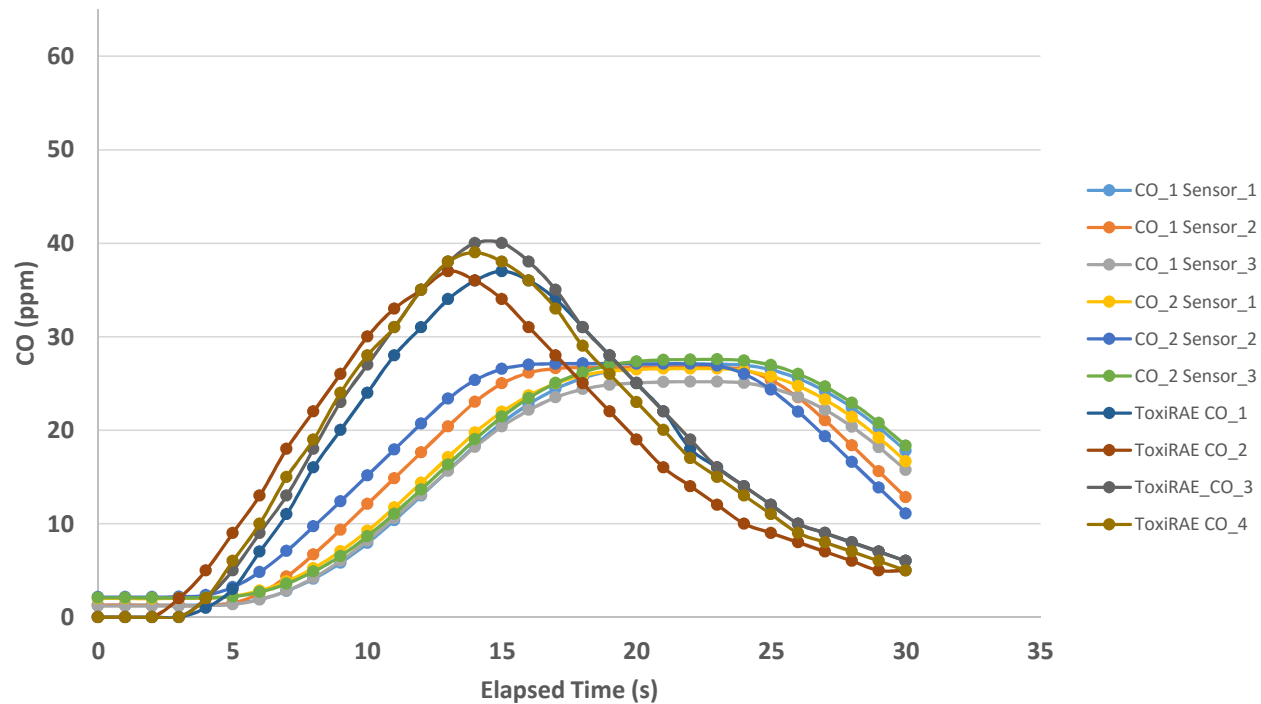
30-s Horiba VA-5111



1.0 L/min Slightly Faster Response
Low reading (47 ppm) Under Vacuum

OVERALL 10 SECOND EVENT

Overall Sensor Response: 10-s

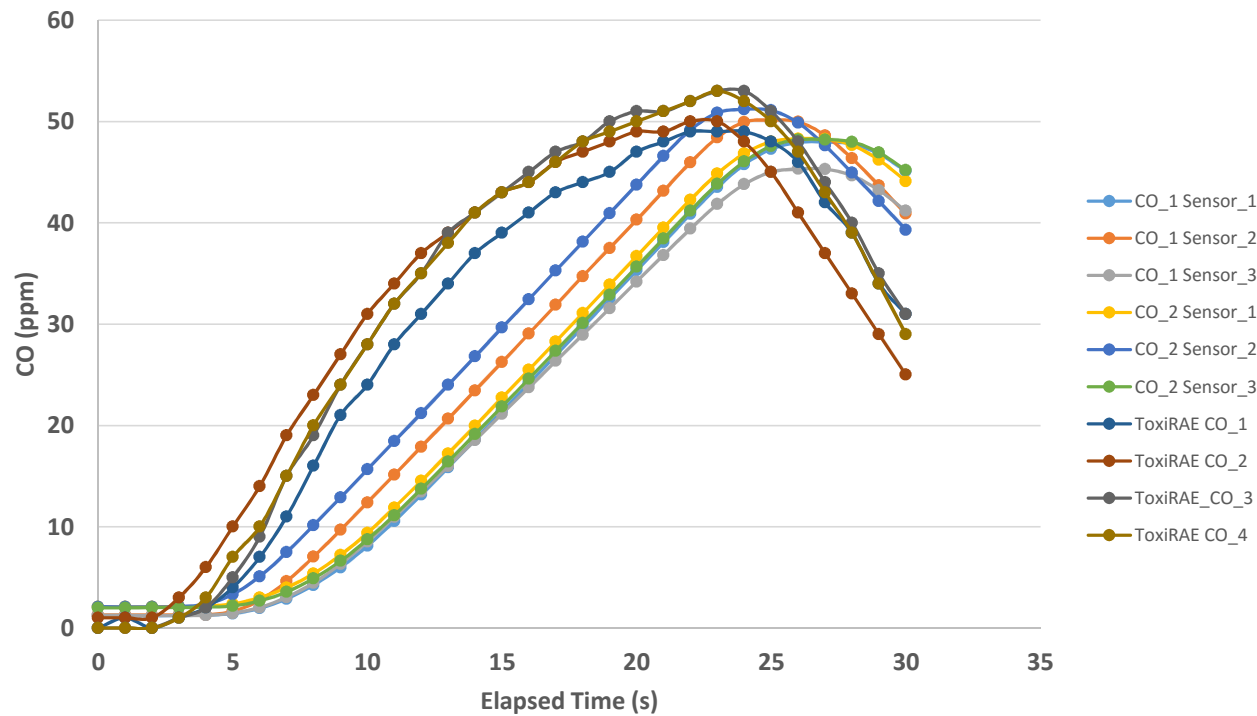


ToxiRAE Had Faster Response



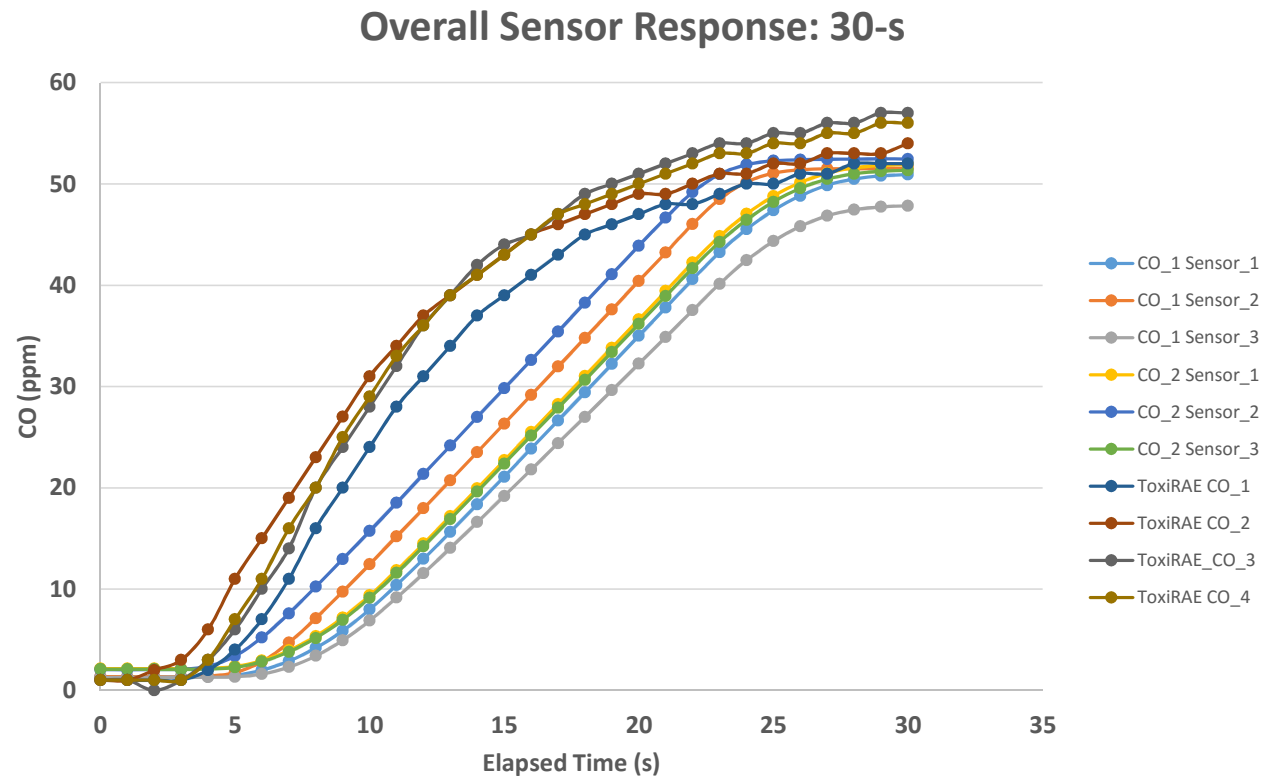
OVERALL 20 SECOND EVENT

Overall Sensor Response: 20-s



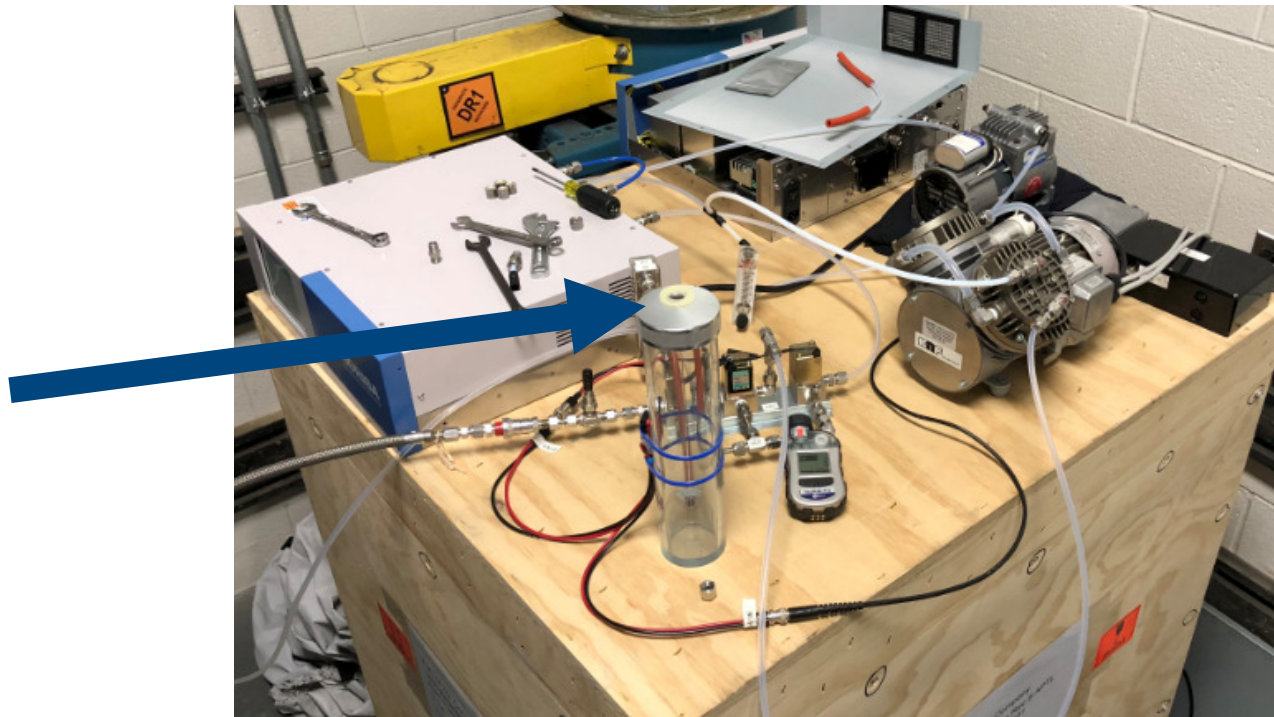
ToxiRAE Had Faster Response; Also Read High (53 ppm)

OVERALL 30 SECOND EVENT



ToxiRAE Had Faster Response; Also Read High (57 ppm)

NEXT STEP - NEW TIME DELAY TEST EQUIPMENT



**Tube In Picture Fills With Gas Then The Sensor Is Quickly Removed From Gas
A Limit Switch Stops The Gas Supply And Turns On Vacuum**

SPECIFICATIONS FOR ZERO GAS (AIR OR N2)

Constituent	Synthetic/Zero Air Purity	Zero Nitrogen Purity	Reference
Nitrogen Oxides (NO _x)	Nitric Oxide (NO) ≤ 0.1 μmol/mol (0.1 ppm)	Nitric Oxide (NO) ≤ 0.1 μmol/mol (0.1 ppm)	US EPA CFR 40 Part 86
Ammonia (NH ₃)	N/A	N/A	
Nitrogen Oxides (NO _x)	≤ 0.02 μmol/mol (20 ppb)	≤ 0.02 μmol/mol (20 ppb)	US EPA CFR 40 Part 1065/1066
Nitrous Oxide (N ₂ O)	≤ 0.02 μmol/mol (20 ppb)	≤ 0.02 μmol/mol (20 ppb)	
Ammonia (NH ₃)	N/A	N/A	
Nitrogen Oxides (NO _x)	Nitric Oxide (NO) ≤ 0.1 μmol/mol (0.1 ppm)	Nitric Oxide (NO) ≤ 0.1 μmol/mol (100 ppb)	WLTP & China 6
Nitrous Oxide (N ₂ O)	≤ 0.1 μmol/mol (0.1 ppm)	Nitrogen Dioxide (NO ₂) < 0.1 μmol/mol (100 ppb)	
Ammonia (NH ₃)	N/A	≤ 0.1 μmol/mol (100 ppb)	

**This Table Is For Reference Only, Level Are Similar To Ambient Levels
Similar Equipment Can Be Used For Table Measurements and VIAQ**



CONVERSION FROM MASS/VOLUME TO PARTS/VOLUME

The molar volume of an ideal gas at 1 atmosphere of pressure:

22.414 L/mol at 0 °C,
24.465 L/mol at 25 °C.

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Russian National Standard GOST R 33554-2015 Limits

	Concentration ppb (mol/mol)	Concentration ppm (mol/mol)	Concentration [μg/m ³]	Concentration [mg/m ³]	Molecular Weight g/mol	Gas Molar Volume L/mol
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Nitrogen Dioxide (NO ₂)	108	0.108	200	0.2	46.01	24.79
Nitric Oxide [NO]	331	0.331	400	0.4	30.01	24.79
Carbon Monoxide [CO]	4425	4.425	5000	5.0	28.01	24.79
Methane [CH ₄]	77275	77.275	50000	50.0	16.04	24.79

Calibration Standards Are Typically Labeled With Volume Concentration



NOX AND NH3 ANALYZERS

Horiba APNA-370

- Chemiluminescence Detector
- Ambient ozone generator
- Measures NO, NO₂, Total NO_x
- 0.1 up to 1.0 ppm ranges
- LOD of 0.5 ppb



Horiba CU-2

- Ammonia converter
- Oxide catalyst for NH₃
- 90% conversion
- Up to 10 ppm converted
- Works in conjunction with APNA-370



Horiba GDC

- MFC based dilution
- LabVIEW VI controlled
- Cutpoints (0%, 5% to 100%)



NO_x MEASUREMENT SETUP FRONT AND BACK



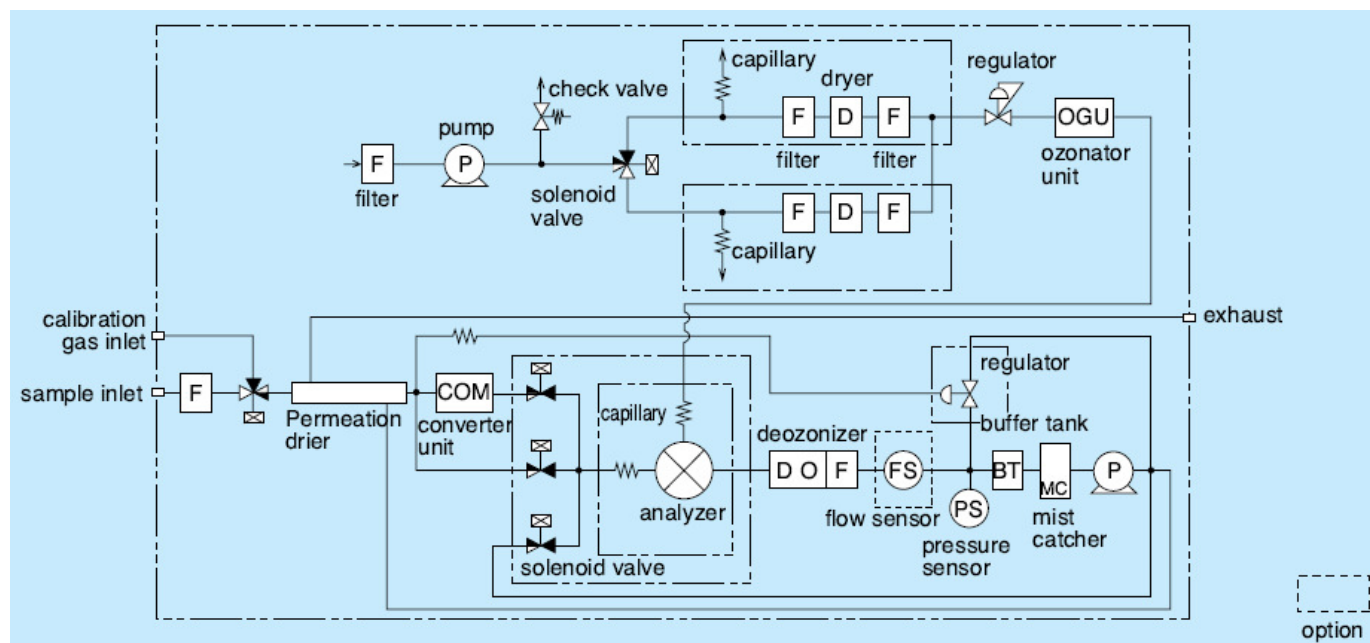
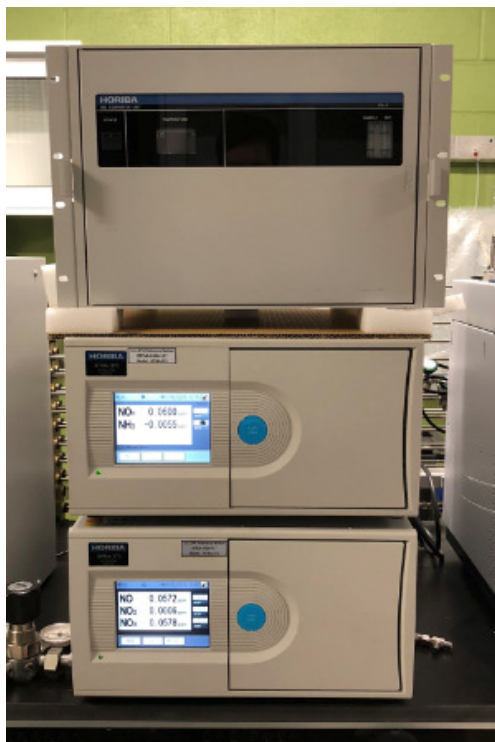
CU-2

(2) APNA

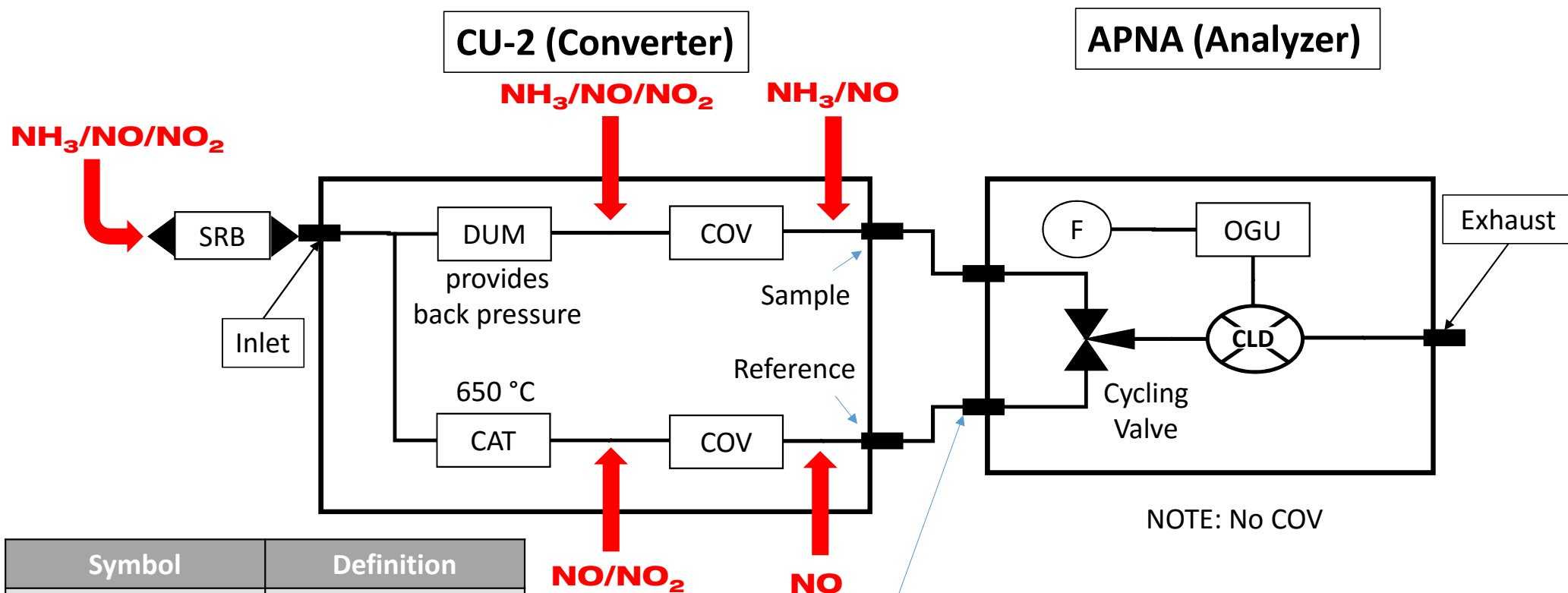
Gas
Divider



Setup of Horiba APNA Units

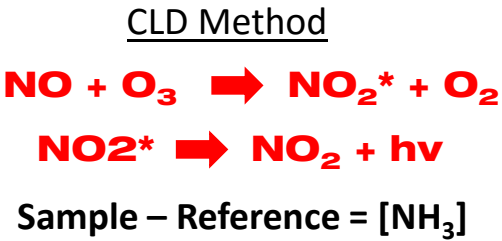


Received 1st (Lower) unit May 11th, 2nd (Upper) unit May 30th
 Diagram is for APNA (NO,NO₂,NO_x), See next slide for (Upper) NH₃ Converter/APNA

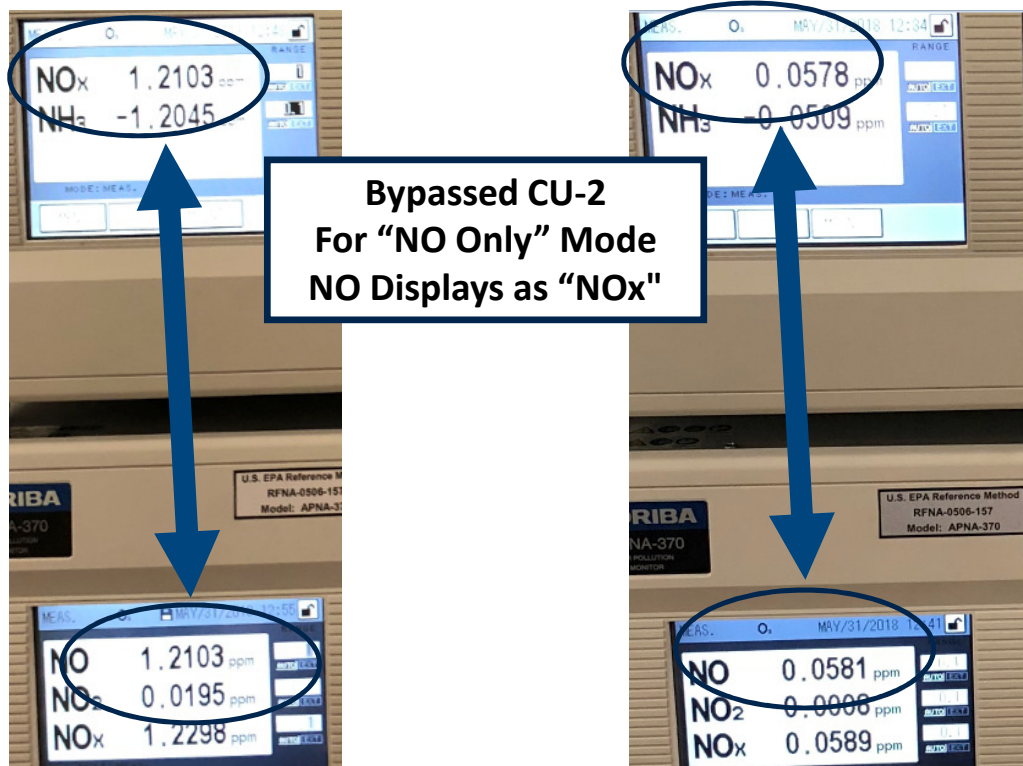


Symbol	Definition
SRB	CS ₂ Scrubber
CAT	Ammonia Catalyst
COV	NO ₂ Converter
F	Filter
OGU	Ozone Generator

For "NO Only" Mode
Bypass CU-2
Displays as "NOx"



READINGS – 100% AND 5% OF 1.255 PPM BOTTLE



100% values the same
down to <0.1 ppb

Parts per Billion!!!

5% bottle values within 3 ppb

Two separate analyzers received weeks apart, factory calibration.
Bottom unit was "ON" from May 11, 2018 to May 31, 2018

CALIBRATION GASES

CERTIFICATE OF ANALYSIS

Grade of Product: TRACEABILITY STANDARD

Part Number: X02NI99T3HAC086 Reference Number: 82-400991268-1A
 Cylinder Number: XN021235B Cylinder Volume: 247.1 CF
 Laboratory: 124 - Riverton (SAP) - NJ Cylinder Pressure: 2215 PSIG
 Valve Outlet: 660
 Certification Date: Nov 13, 2017

Expiration Date: Nov 13, 2020

This cylinder has been analytically certified as directly traceable to NIST with a total analytical uncertainty as stated below with a confidence level of 95%, in accordance with Airgas ISO procedures. There are no significant impurities which affect the use of this calibration mixture. All concentrations are on a volume/volume basis unless otherwise noted.

Do Not Use This Cylinder Below 100 psig

ANALYTICAL RESULTS			
Component	Requested Concentration	Actual Concentration	Total Relative Uncertainty
NOx		1.267 PPM	+/- 1% NIST Traceable
NITRIC OXIDE	1.000 PPM	1.255 PPM	+/- 1% NIST Traceable
NITROGEN	Balance		
Total oxides of nitrogen		1.267 PPM	For Reference Only

CALIBRATION STANDARDS					
Type	Lot ID	Cylinder No	Concentration	Uncertainty	Expiration Date
SRM	2738-AL-26	AAL069215	1.066 PPM NITRIC OXIDE/NITROGEN	+/- 1.4%	Sep 06, 2019
SRM	2738-AL-26	AAL069215-NOX	1.067 PPM NOx/NITROGEN	+/- 1.4%	Sep 06, 2019

ANALYTICAL EQUIPMENT		
Instrument/Make/Model	Analytical Principle	Last Multipoint Calibration
Thermo 42i-LS-NO-1123749326	Chemiluminescence	Oct 13, 2017
Thermo 42i-LS-NOx-1123749326	Chemiluminescence	Oct 13, 2017

Triad Data Available Upon Request

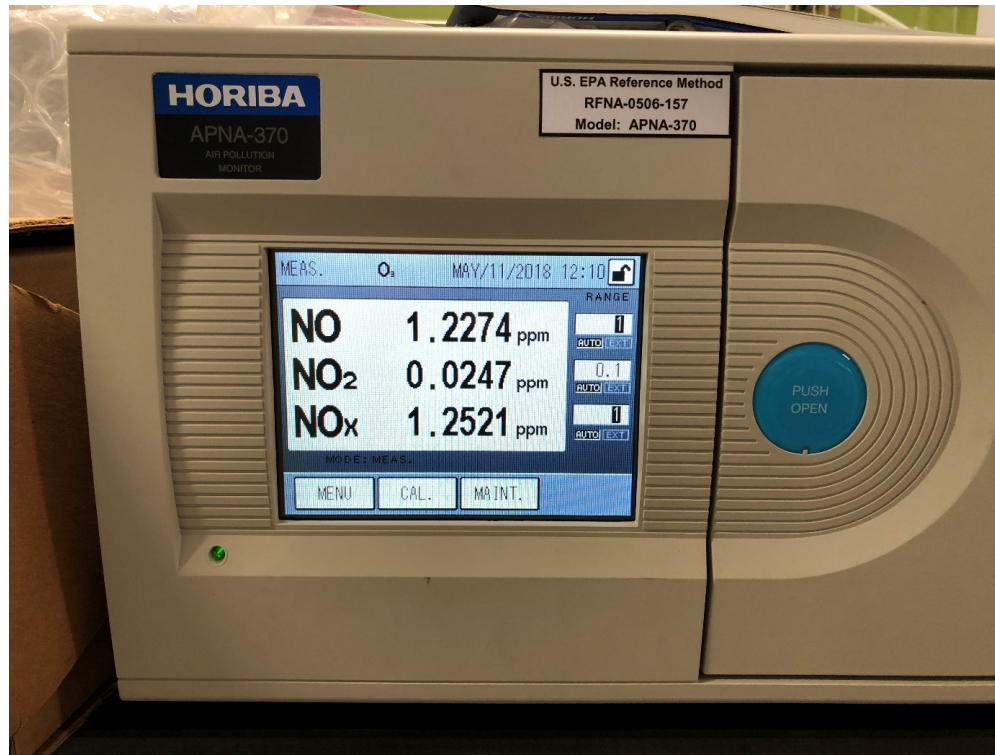
PERMANENT NOTES: COMPLIES WITH 40 CFR PART 1065.750



1.255 NO, 1% NIST Traceable



Traceable Bottle Read ($1.255 \text{ NO} + 0.012 \text{ NO}_2 = 1.267 \text{ NO}_x$)



Accuracy = NO @ 2.2% and Nox @ 1.2%, New Bottle and Factory Calibration

CALIBRATION GASES



Airgas Specialty Gases
Airgas USA, LLC
630 United Drive
Durham, NC 27713
Airgas.com

CERTIFICATE OF ANALYSIS

Grade of Product: PRIMARY STANDARD

Part Number:	X02NI99P3HA0045	Reference Number:	122-401034134-1
Cylinder Number:	ND43443	Cylinder Volume:	247.1 CF
Laboratory:	124 - Durham (SAP) - NC	Cylinder Pressure:	2215 PSIG
Analysis Date:	Oct 25, 2017	Valve Outlet:	590
Lot Number:	122-401034134-1		

Primary Standard Gas Mixtures are traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials.

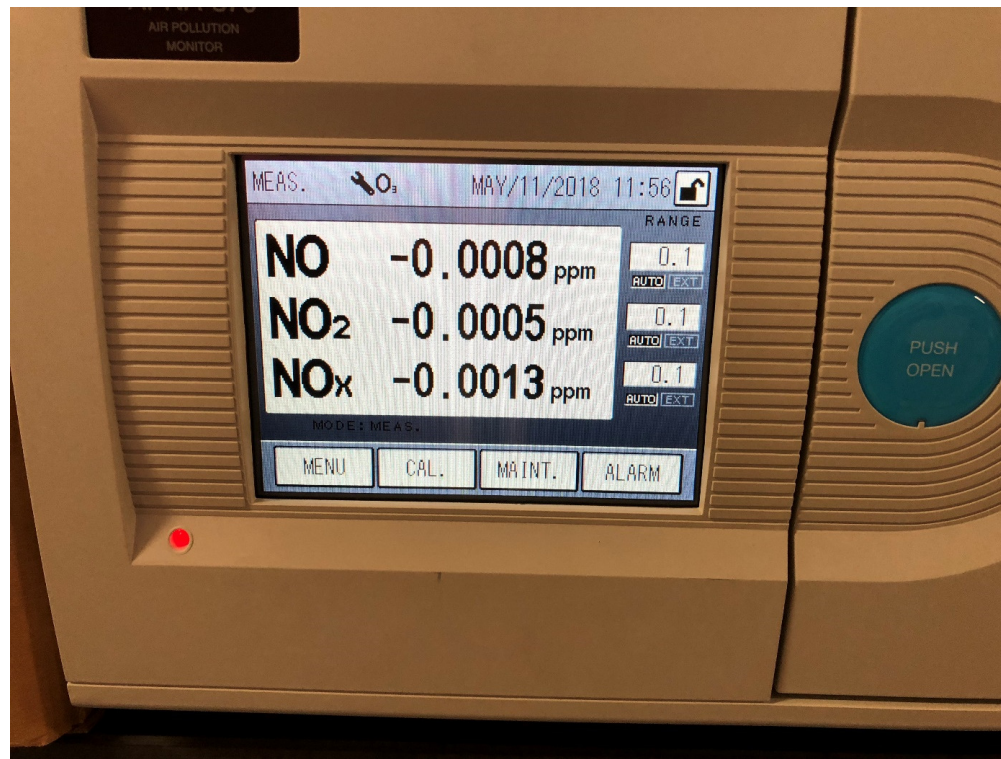
ANALYTICAL RESULTS

Component	Req Conc	Actual Concentration (Mole %)	Analytical Uncertainty
NITROUS OXIDE	0.2000 PPM	0.1890 PPM	+/- 5%
NITROGEN	Balance		

0.1890 PPM +/-5%



WHAT HAPPENED? NEED TO RECHECK THE LABEL!



The bottle was Nitrous Oxide (N_2O).
The good result, zero NO_x Present.

CALIBRATION GASES



Airgas Specialty Gases
Airgas USA, LLC
630 United Drive
Durham, NC 27713
Airgas.com

CERTIFICATE OF ANALYSIS Grade of Product: PRIMARY STANDARD

Part Number:	X05AI99P3HA0001	Reference Number:	122-401036053-1
Cylinder Number:	GN0001749	Cylinder Volume:	250.8 CF
Laboratory:	124 - Durham (SAP) - NC	Cylinder Pressure:	2215 PSIG
Analysis Date:	Oct 26, 2017	Valve Outlet:	590
Lot Number:	122-401036053-1		

Primary Standard Gas Mixtures are traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials.

ANALYTICAL RESULTS

Component	Req Conc	Actual Concentration (Mole %)	Analytical Uncertainty
NITROUS OXIDE	0.2000 PPM	0.1830 PPM	+/- 5%
METHANE	0.5000 PPM	0.4694 PPM	+/- 5%
CARBON MONOXIDE	10.00 PPM	9.976 PPM	+/- 2%
CARBON DIOXIDE	100.0 PPM	99.51 PPM	+/- 1%
AIR	Balance		

Same thing here Nitrous Oxide (N₂O) but includes other gases
There could be a blend that would work for all calibration compounds



CALIBRATION GASES



Airgas Specialty Gases
Airgas USA, LLC
600 Union Landing Road
Cinnaminson, NJ 08077-0000
Airgas.com

CERTIFICATE OF ANALYSIS

Grade of Product: PRIMARY STANDARD

Part Number:	X02NI99P15A01H2	Reference Number:	82-401051019-1
Cylinder Number:	CC437476	Cylinder Volume:	144.3 Cubic Feet
Laboratory:	124 - Riverton (SAP) - NJ	Cylinder Pressure:	2015 PSIG
Analysis Date:	Dec 14, 2017	Valve Outlet:	660
Lot Number:	82-401051019-1		

Primary Standard Gas Mixtures are traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials.

ANALYTICAL RESULTS

Component	Req Conc	Actual Concentration (Mole %)	Analytical Uncertainty
NITRIC OXIDE	0.2000 PPM	0.2200 PPM	+/- 5%
NITROGEN	Balance		
Total oxides of nitrogen		0.2200 PPM	For Reference Only

Second NO standard, 0.2200 ppm +/-5%



CALIBRATION GASES



Airgas Specialty Gases
Airgas USA, LLC
6141 Easton Road
Bldg 1
Plumsteadville, PA 18949
Airgas.com

CERTIFICATE OF ANALYSIS

Grade of Product: CERTIFIED STANDARD-SPEC

Customer:	FORD ALLEN PARK TEST LAB	Reference Number:	160-401016823-1
Part Number:	X02NI99C3HA00B3	Cylinder Volume:	244 CF
Cylinder Number:	ND61384	Cylinder Pressure:	2200 PSIG
Laboratory:	124 - Plumsteadville - PA	Valve Outlet:	705
Analysis Date:	Nov 10, 2017		
Lot Number:	160-401016823-1		

Expiration Date: Nov 10, 2018

Product composition verified by direct comparison to calibration standards traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials.

ANALYTICAL RESULTS

Component	Req Conc	Actual Concentration (Mole %)	Analytical Uncertainty
AMMONIA	0.5000 PPM	0.4830 PPM	+/- 5%
NITROGEN	Balance		

0.4830 ppm +/-5% Ammonia (NH₄)

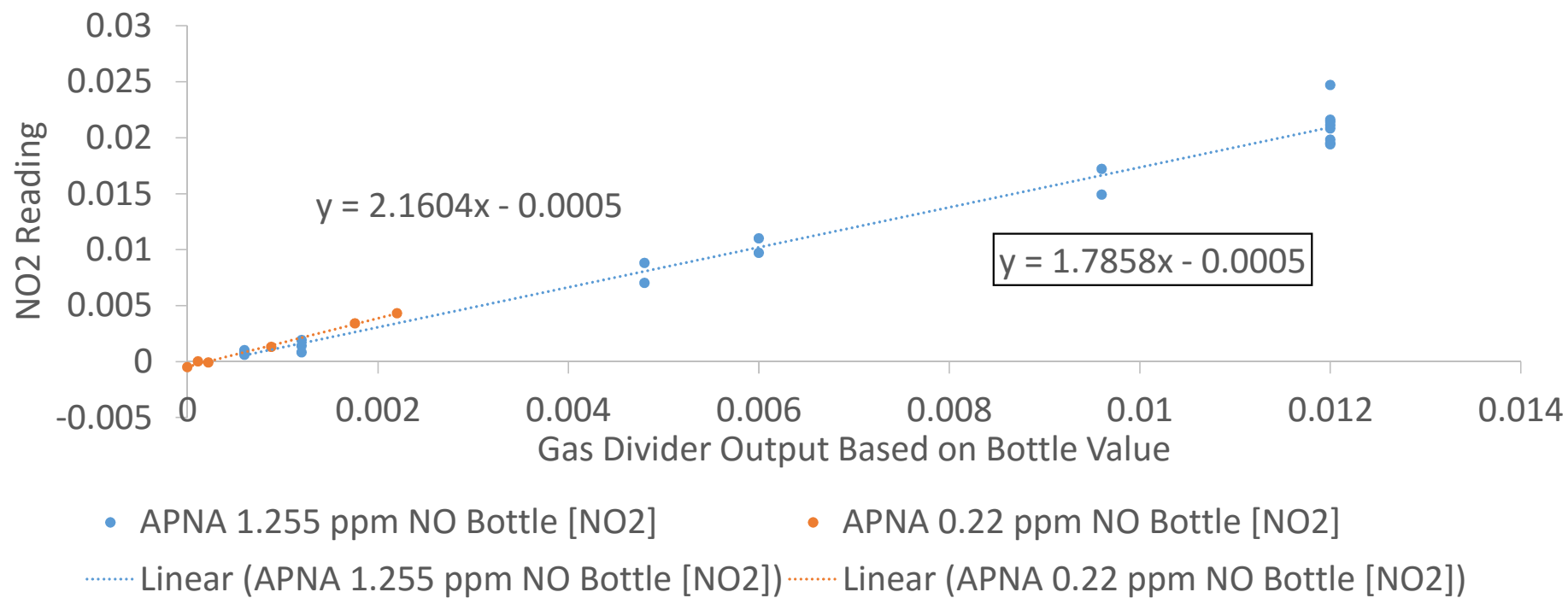


TEST PLAN

- Sample Standard “NO” Direct from New Bottle with Overflow
- Sample Standard “NO” With Gas Divider
 - Moving output of gas divider between analyzers (back and forth)
 - » This caused the MFCs in the gas divider to re-find flow value
 - Keeping the output of gas divider flowing to both analyzers at the same time
 - » This was a comparison between the two analyzers
- Sample Standard “NH₃” using the CU-2, NOT A TAILPIPE REQUIREMENT

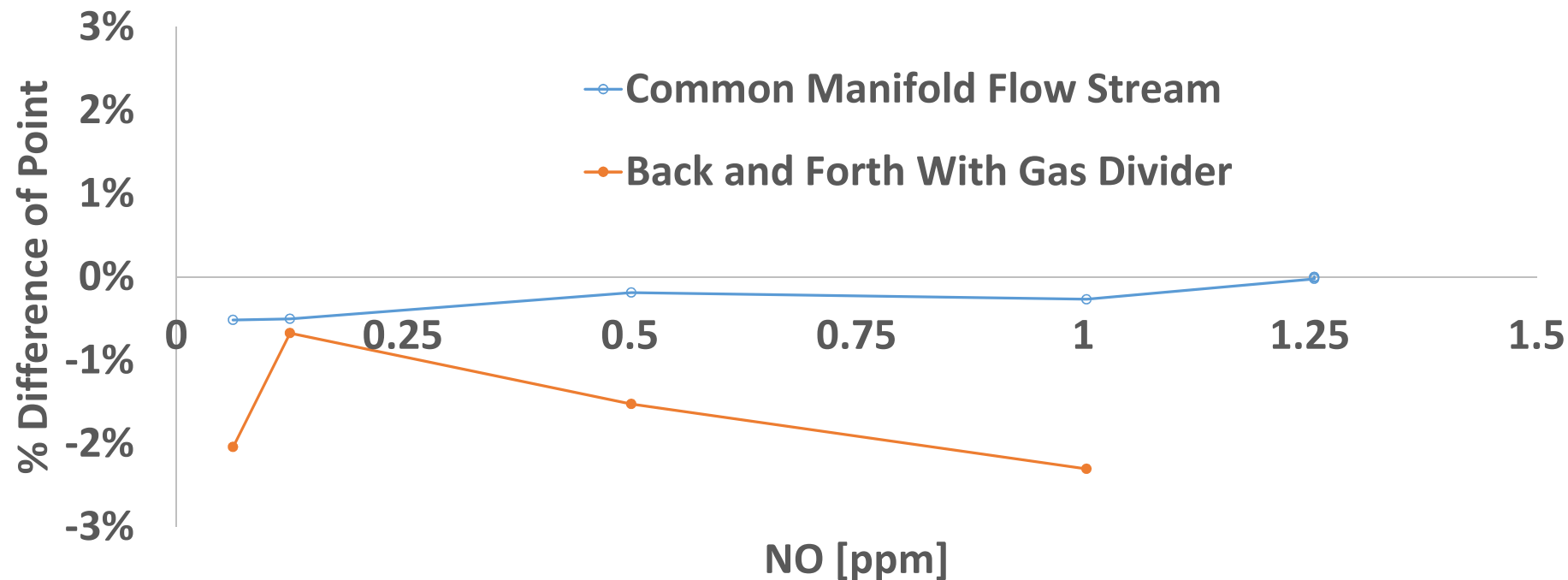
This test plan was run over three days

NO₂ READINGS FROM APNA



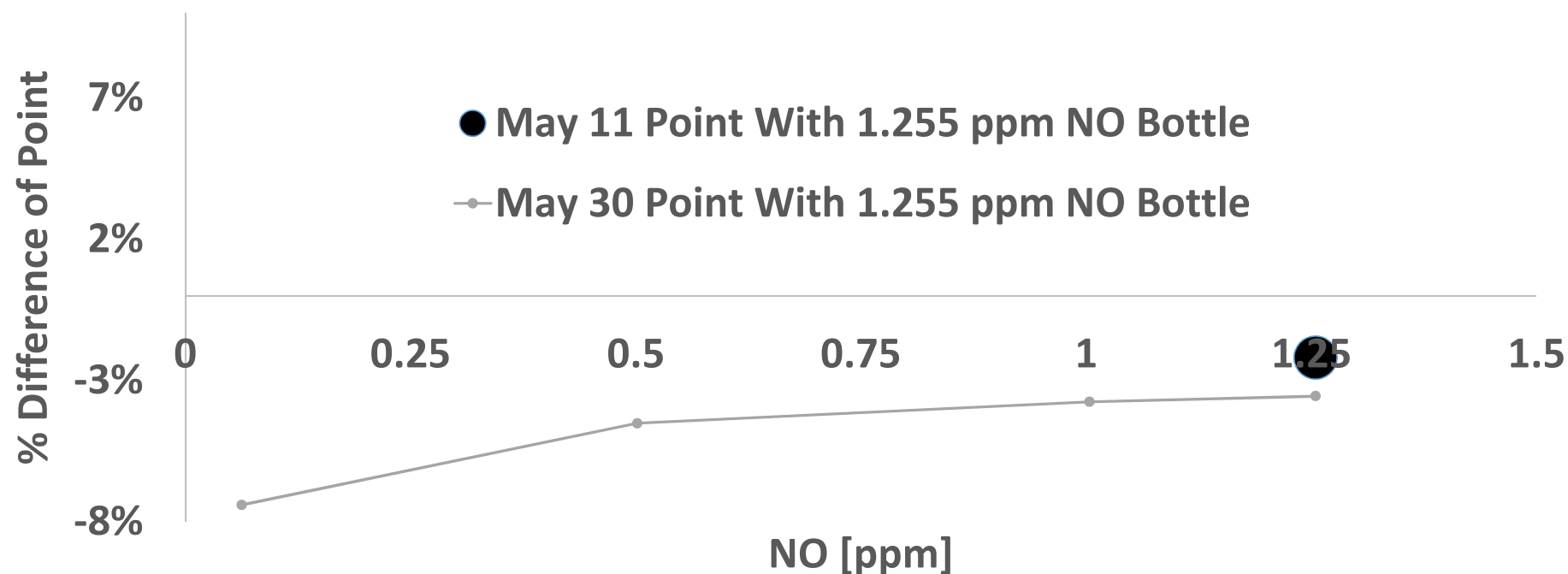
**Based On Two Bottles The NO₂ Is Low, About 1% Of NO Label Concentration
Data Showed Good Linear Response, Offset Likely Due To Bottle Label**

TWO APNAS READING THE SAME GAS STREAM



**One APNA Received May 11 Another on May 30, Both With Factory Calibration
Disconnecting And Reconnecting The Gas Divider Is Not As Repeatable**

% DIFFERENCE APNA VS. LABEL CONCENTRATIONS



There Was A Shift Over Time That Is Unexplained. The APNA Still Has The Factory Calibration And Was “ON” The Whole Time Between Readings.

Conclusions and Next Steps

- **ToxiRAE**
 - Passive inlet showed faster response due to gas forced onto sensor thus not consistent with a normal testing scenario
 - A more representative sampling system has been developed to mimic testing events
- **Horiba**
 - Instrument was not calibrated to negative pressure and lead to low readings when vacuum was applied, need to calibrate under testing conditions
 - Working with Horiba to change response time electronically, adjust averaging calculations
- **NOx measurements precautions to consider when testing**
 - Ensuring no oxygen back flushing into analyte bottle can occur
 - NO concentration depletion control, should add process to insure calibration gas is stable
 - Could pump-down regulator to ensure no oxygen contamination
 - Periodic bottle mixing for could help low concentrations are stable and homogeneous
- **NIST visit in September to discuss gas handling, bottle naming and calibration procedures**
- **Much more testing planned...**

