CALIBRATION GAS MANUFACTURING:

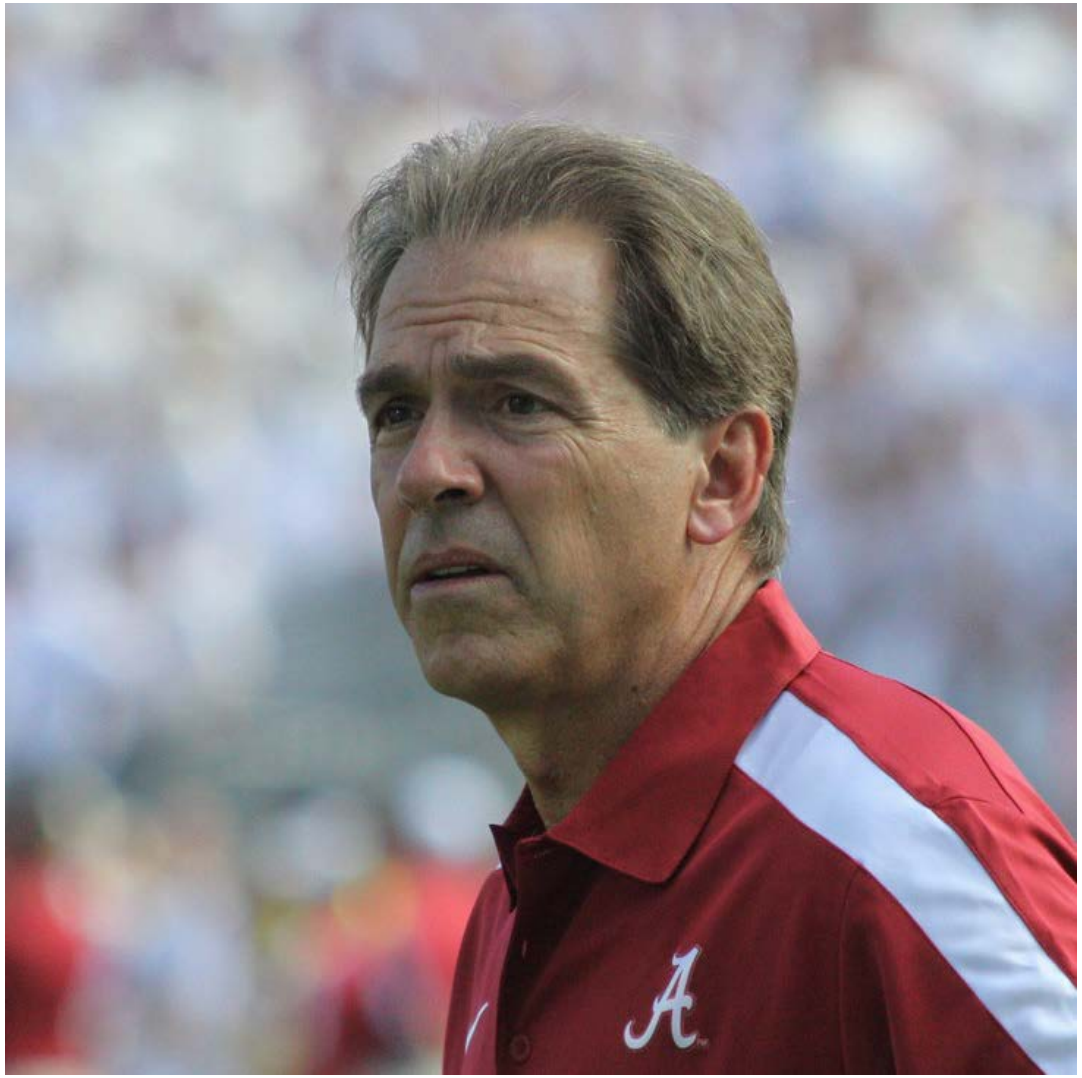
ENSURING PRECISION IN ENVIRONMENTAL COMPLIANCE

Mark Patten | Vice President Of Technical Gas Services

RED BALL
TECHNICAL GAS SERVICES

“The Process is really what you have to do day in and day out to be successful.”

NICK SABAN



EXPLORING THE CRUCIAL ROLE OF EPA PROTOCOL CALIBRATION GASES

- EPA Protocol Gases: Essential for Precision-Demand Industries
- Supporting Environmental Compliance Through Gas Manufacturing
- Aiding Emission Reporting in Environmental and Stationary Analysis.
- Participation in EPA's PGVP Mandatory for Manufacturers; 27 Sites Listed as of 2023

OVERVIEW OF CALIBRATION GAS MANUFACTURING

STEP 1

- **Accurately receiving and reentering customer orders**

CONSIDERATIONS:

- Meeting Manufacturer's Blend Tolerances
- Assessing Mixture Component Compatibility
- Correct Cylinder and CGA Valve Identification
- Ensuring Safe Blending
- Product Compliance and Customer Satisfaction

RECIPE GENERATION AND CYLINDER PROCESSING

STEP 2

- Create fill recipe: correct cylinder, CGA valve. Recipe generation in grams or kilograms
- Verify cylinder's proper pre-fill processing.
- Evacuation/Bake Out and Passivation steps (Manufacturer Specific)
- Introducing minor components: Direct Add or Base Mixture.
- Daily scale check: NIST-certified, high precision
- Example: Sartorius scales (0.1g floor, 0.01g bench)

CYLINDER SIZE SPECIFICATIONS

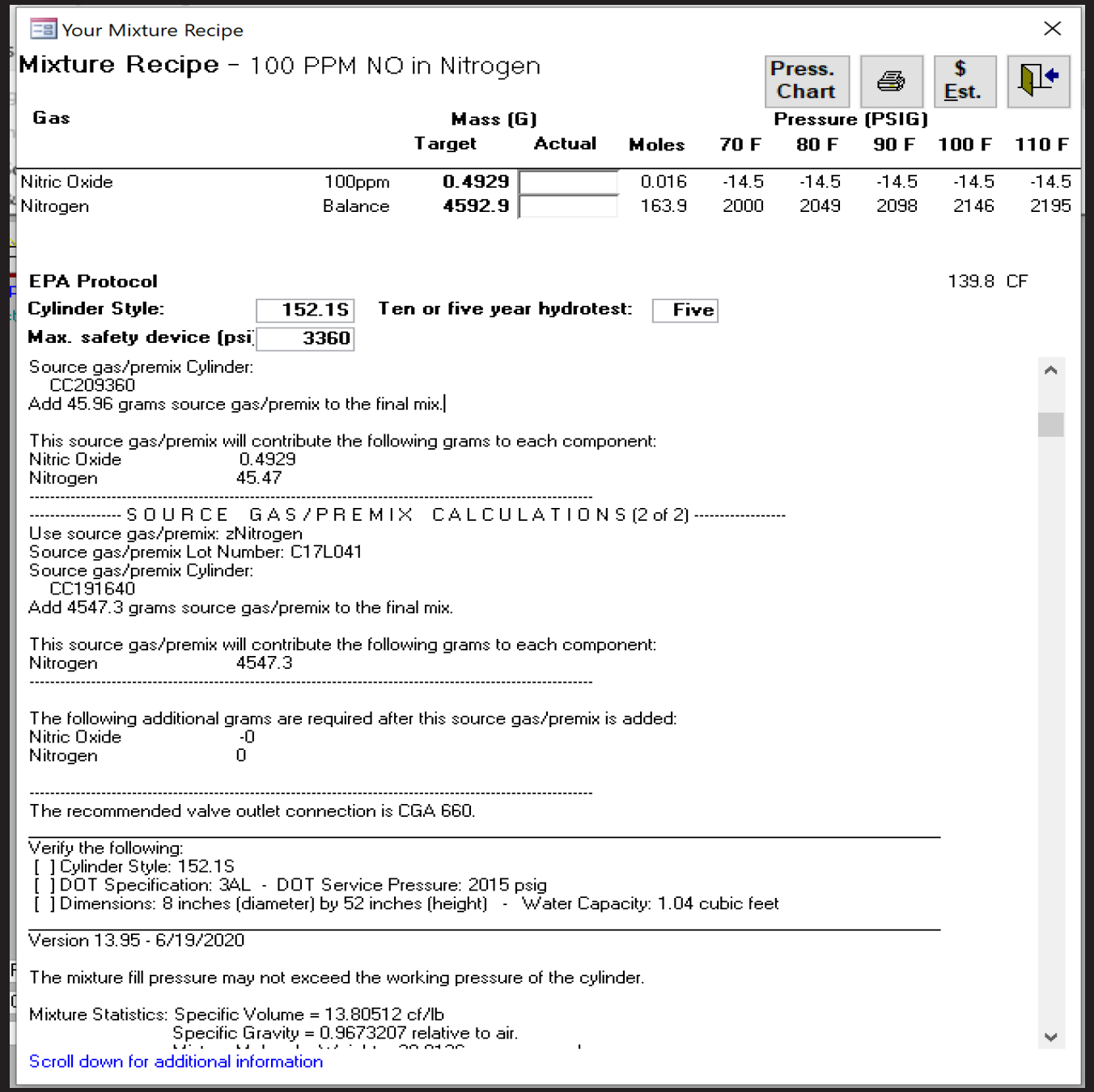
Cyl. Size	Nominal Size* Dia X Height (inches)	Nominal* Tare Weight (lbs.)	Water Capacity (lbs.)	Internal Volume @ 70° F (21° C), 1 ATM (liters/cubic feet)		US DOT Specs
300	9.25 X 60	135	110	49.9	1.76	3AA2400
200	9 X 56	115	96	43.8	1.55	3AA2015
80	8.5 X 31	60	37.9	17.2	0.61	3AA2015
40	6 X 24	27	15.2	6.88	0.24	3AA2015
20	4 X 18	12	4.9	2.24	0.08	3AA2015
152	8 X 53	52	64.8	29.5	1.04	3AL2015
82	7.25 X 39	33	34.6	15.7	0.55	3AL2216
32	6.9 X 21	19	13	5.9	0.21	3AL2216
LP239	14.5 X 50	75	238	108	3.83	4BA240
SSB	8 X 37	95	41.6	18.9	0.67	3A1800
10S	4 X 31	21	8.3	3.8	0.13	3A1800
LB	2 X 15	4	1	0.44	0.016	3E1800
XF	12 X 46	180	--	60.9	2.15	8AL
XG	15 X 56	149	278	126.3	4.46	4AA480
XM	10 X 49	90	120	54.3	1.92	3A480
XP	10 X 55	55	124	55.7	1.98	4BA300
QT	3 X 14**	2.5**	2.0	0.900	0.0318	4B-240ET
LP5	12.25 X 18.25	18.5	47.7	21.68	0.76	4BW240

STANDARD CYLINDER SIZES

*Includes 5.5 inches or 4.5 lbs. for valve and cap

**Includes 4.5 inches or 1.5 lbs. for valve

EXAMPLE OF RECIPE: 100 PPM NITRIC OXIDE IN NITROGEN



Your Mixture Recipe

Mixture Recipe – 100 PPM NO in Nitrogen

Press. Chart | $ Est.

Gas		Mass (G) Target	Actual	Moles	Pressure (PSIG) 70 F	80 F	90 F	100 F	110 F
Nitric Oxide	100ppm	**0.4929**		0.016	-14.5	-14.5	-14.5	-14.5	-14.5
Nitrogen	Balance	**4592.9**		163.9	2000	2049	2098	2146	2195

EPA Protocol 139.8 CF

Cylinder Style: 152.1S **Ten or five year hydrotest:** Five

Max. safety device (psi 3360

Source gas/premix Cylinder:
CC209360
Add 45.96 grams source gas/premix to the final mix.

This source gas/premix will contribute the following grams to each component:
Nitric Oxide 0.4929
Nitrogen 45.47

---------- S O U R C E G A S / P R E M I X C A L C U L A T I O N S (2 of 2) ----------
Use source gas/premix: zNitrogen
Source gas/premix Lot Number: C17L041
Source gas/premix Cylinder:
CC191640
Add 4547.3 grams source gas/premix to the final mix.

This source gas/premix will contribute the following grams to each component:
Nitrogen 4547.3

The following additional grams are required after this source gas/premix is added:
Nitric Oxide -0
Nitrogen 0

The recommended valve outlet connection is CGA 660.

Verify the following:
[ ] Cylinder Style: 152.1S
[ ] DOT Specification: 3AL - DOT Service Pressure: 2015 psig
[ ] Dimensions: 8 inches (diameter) by 52 inches (height) - Water Capacity: 1.04 cubic feet

Version 13.95 - 6/19/2020

The mixture fill pressure may not exceed the working pressure of the cylinder.

Mixture Statistics: Specific Volume = 13.80512 cf/lb
Specific Gravity = 0.9673207 relative to air.

Scroll down for additional information

FILLING PROCESS

STEP 3

- Begin filling process
  - Connect selected cylinders to fill system
  - Evacuate system to remove impurities
  - Add minor and balance components as per recipe
  - Component addition: Direct or base-mixture methods
  - Repeat steps for each component addition
  - Post-fill: Roll or shake for mixture homogeneity
  - Prepare filled cylinders for testing process

BAKE OUT SYSTEM

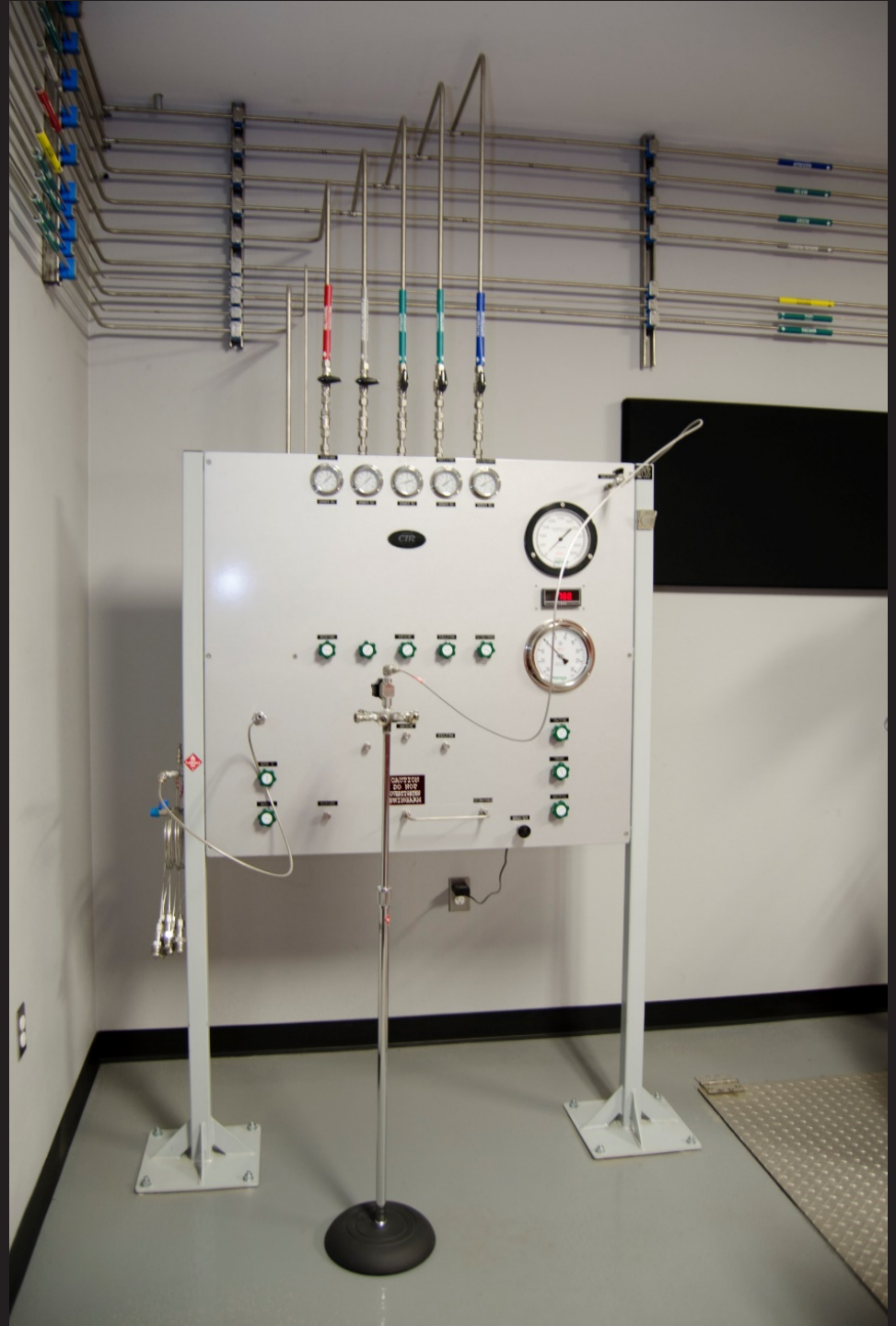
BLOW DOWN PREP MANIFOLD


OXIDIZER
FILL ROOM
RED
TECHNICAL GAS
800-551-8150

FILLLING SYSTEMS


FLAMMABLE BLENDING
VENT
VACUUM
FILL
METERING
HYDROGEN
METHANE
HELIUM
ARGON
NITROGEN
ON
OFF
RED BALL


RED BALL



CYLINDER INVERTER

SIX CYLINDER CAPACITY

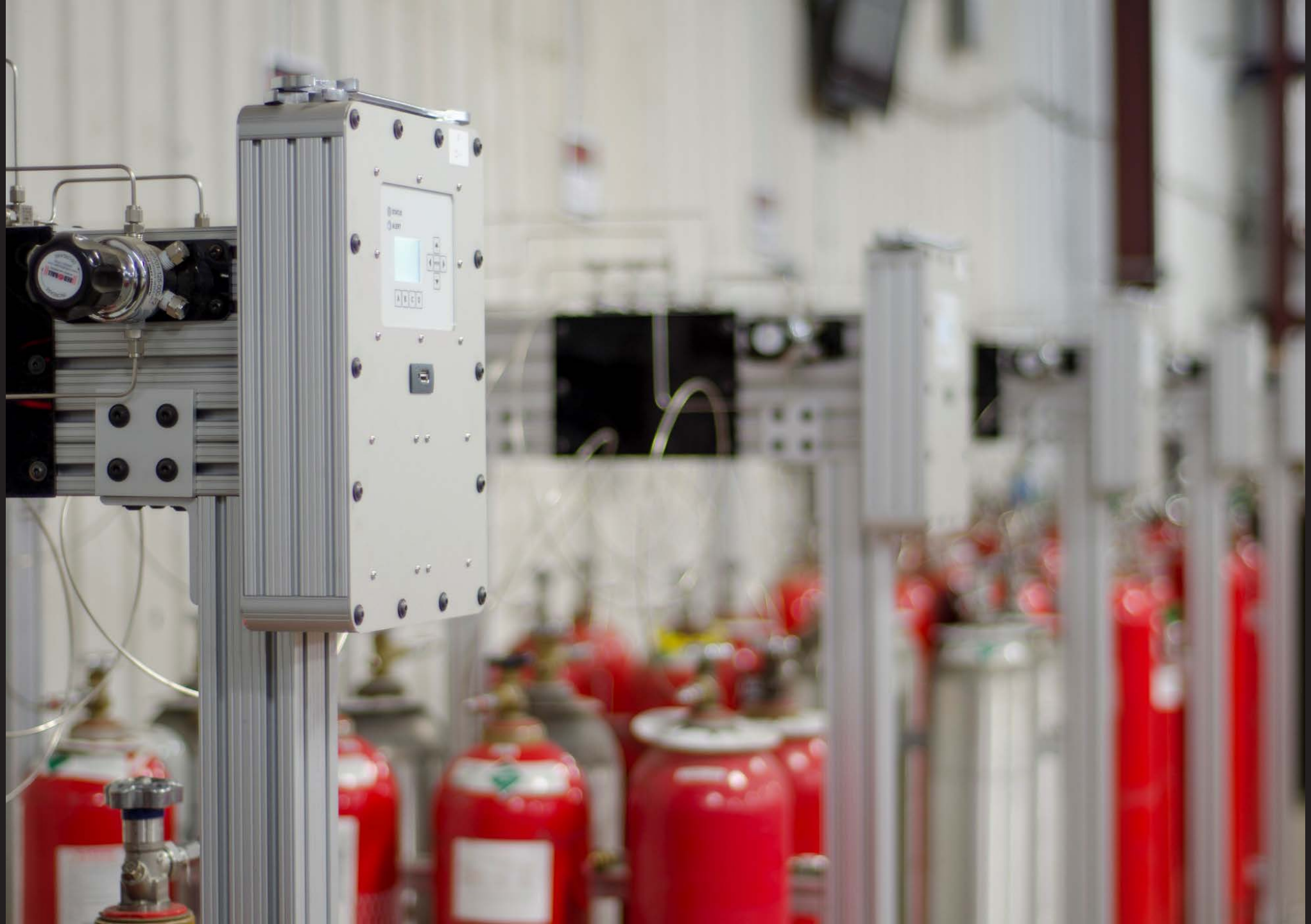
MULTI-POINT CALIBRATION FUNDAMENTALS

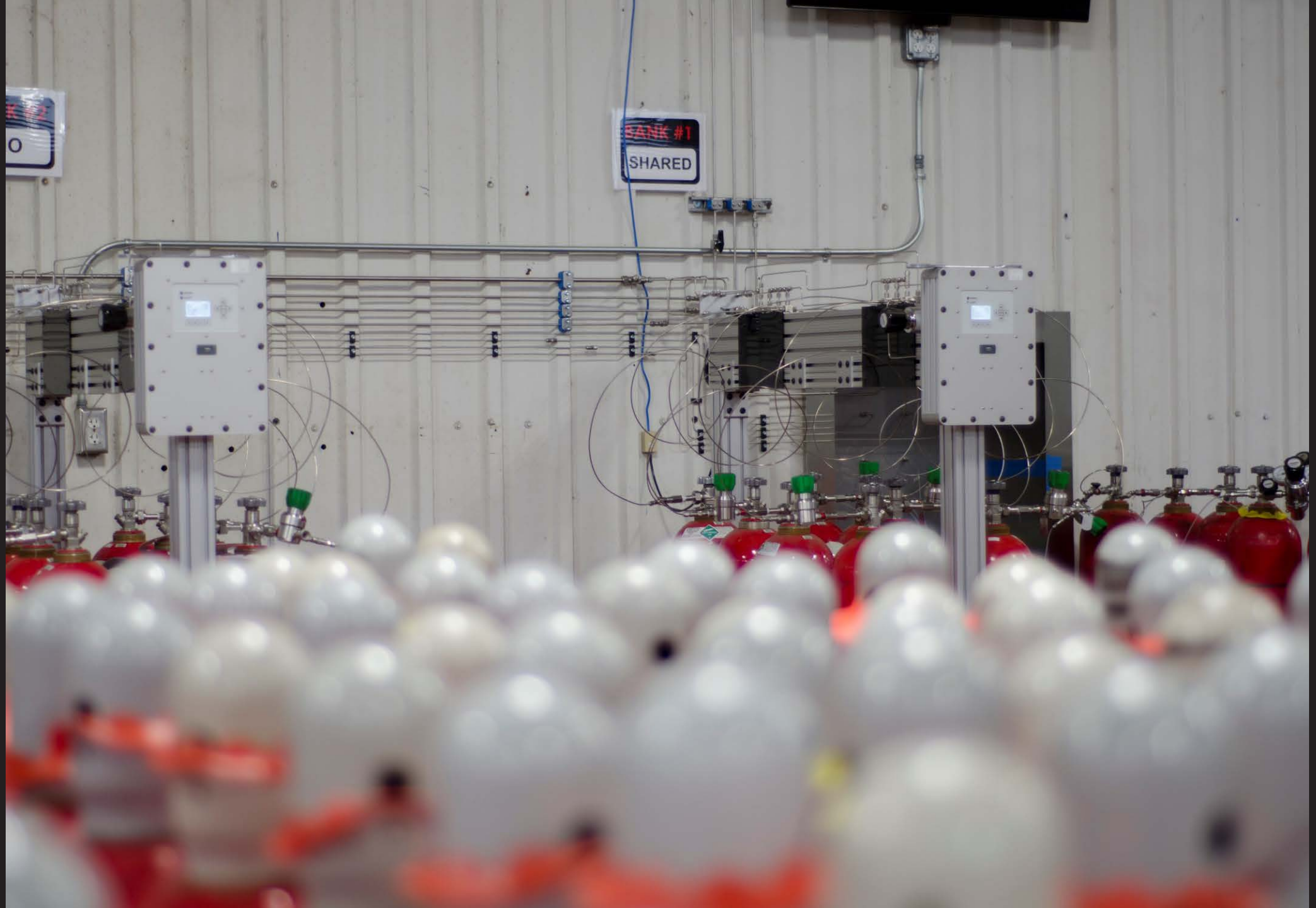
- Calibration every 30 days for precision
- Adjusts for operational range changes
- Daily 5% relative difference checks
- Monthly recalibration with new curves
- Ensures instrument adapts to range shifts
- Daily checks maintain ongoing accuracy

TESTING PROCESS

- Initiate standardized testing protocols
- Conducting leak detection tests
- Performing gas mixture analysis
- Verifying compliance with quality standards
- Cross-checking with recipe specifications
- Recording test results for traceability
- Ensuring consistency in repeat tests


BANK #2
NO
BANK #3
SO2




BANK #1
SHARED

TESTING AND CERTIFICATION

- 4-day incubation period for samples.
- Three assays against NIST Reference Material/equivalent
- Requirement for valid multi-point analysis
- Daily span checks for validity.
- Utilizing TOST statistical model
- 7-day (11 total days) stability period for reactive gases
- Overlap in results leads to cylinder certification
- Non-overlap: Repeat process and certify/disqualify
- Assign expiration date, label, and certification paperwork

ANALYZER BANKS WITH FLOW CONTROL SYSTEMS

SEPARATE LAB SETUPS

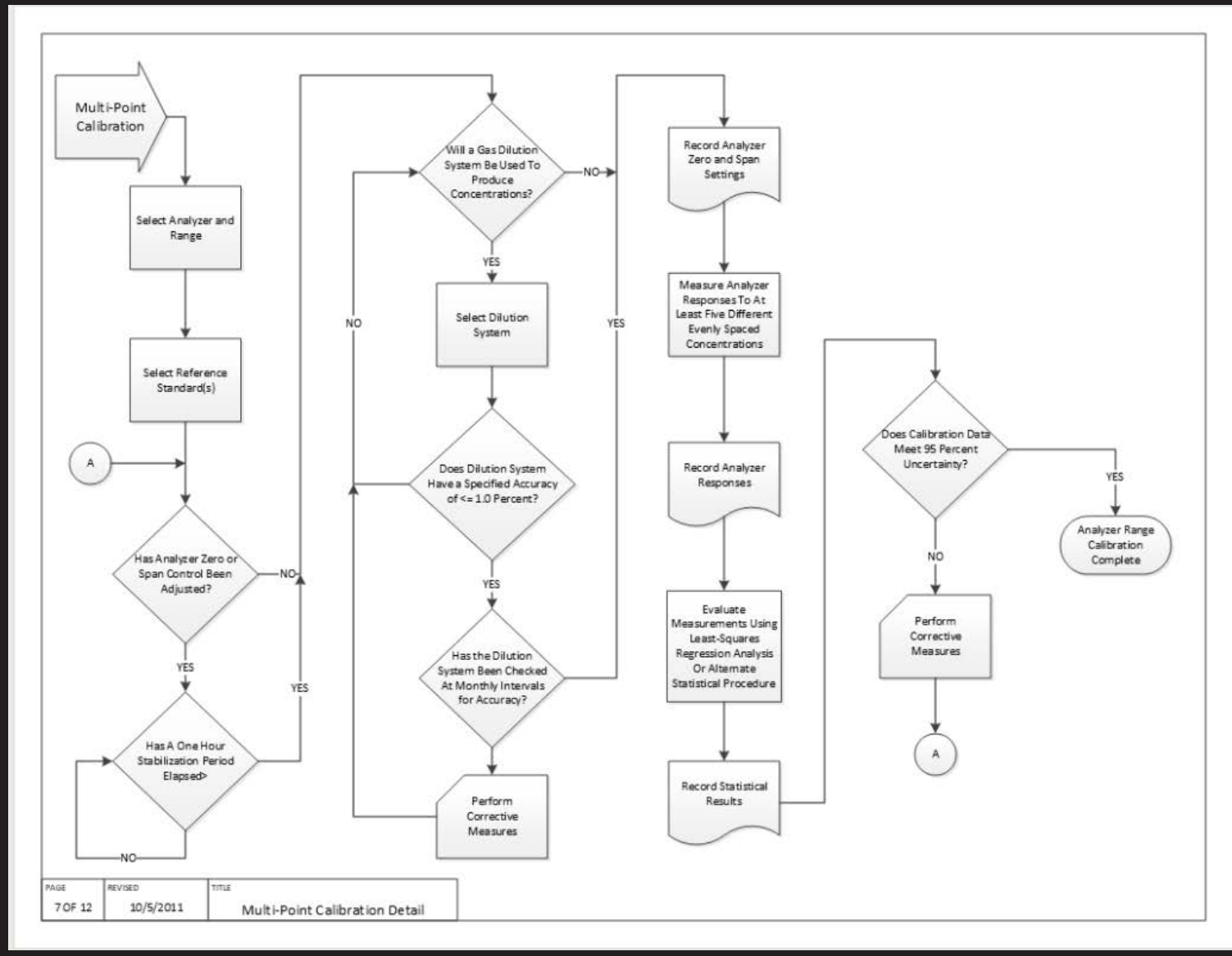
MICRO LAB DESIGN


RED BALL
TECHNICAL GAS SERVICES
acer

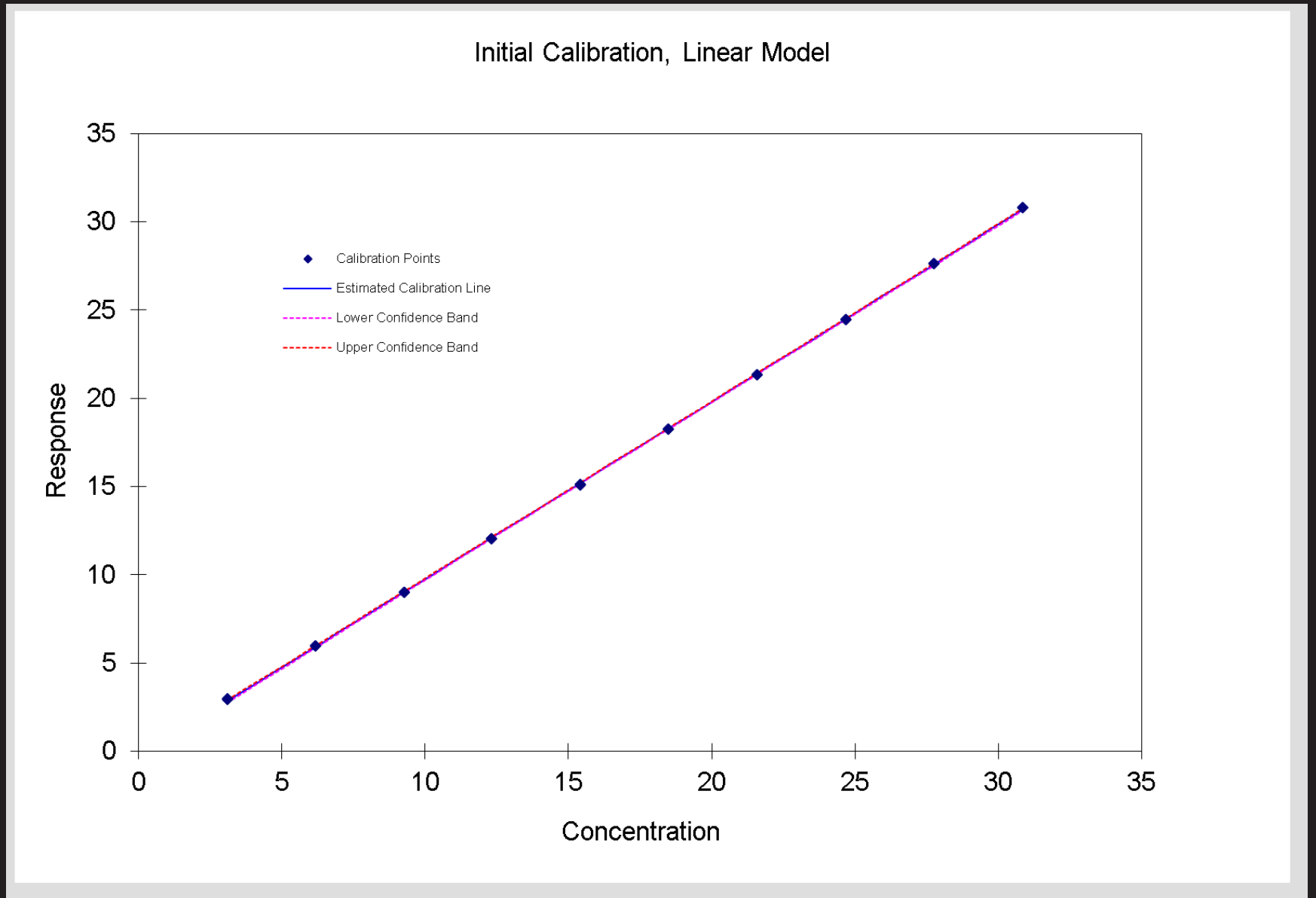
EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF GASEOUS CALIBRATION STANDARDS

- Overview of EPA Green Book Protocols
- Assay Procedures for Gaseous Calibration Standards
- Certification Processes under EPA Guidelines
- Ensuring Traceability in Gas Calibration
- Adherence to Environmental Compliance Standards
- Quality Assurance in Calibration Gas Production
- Documentation and Record-Keeping for EPA Certification

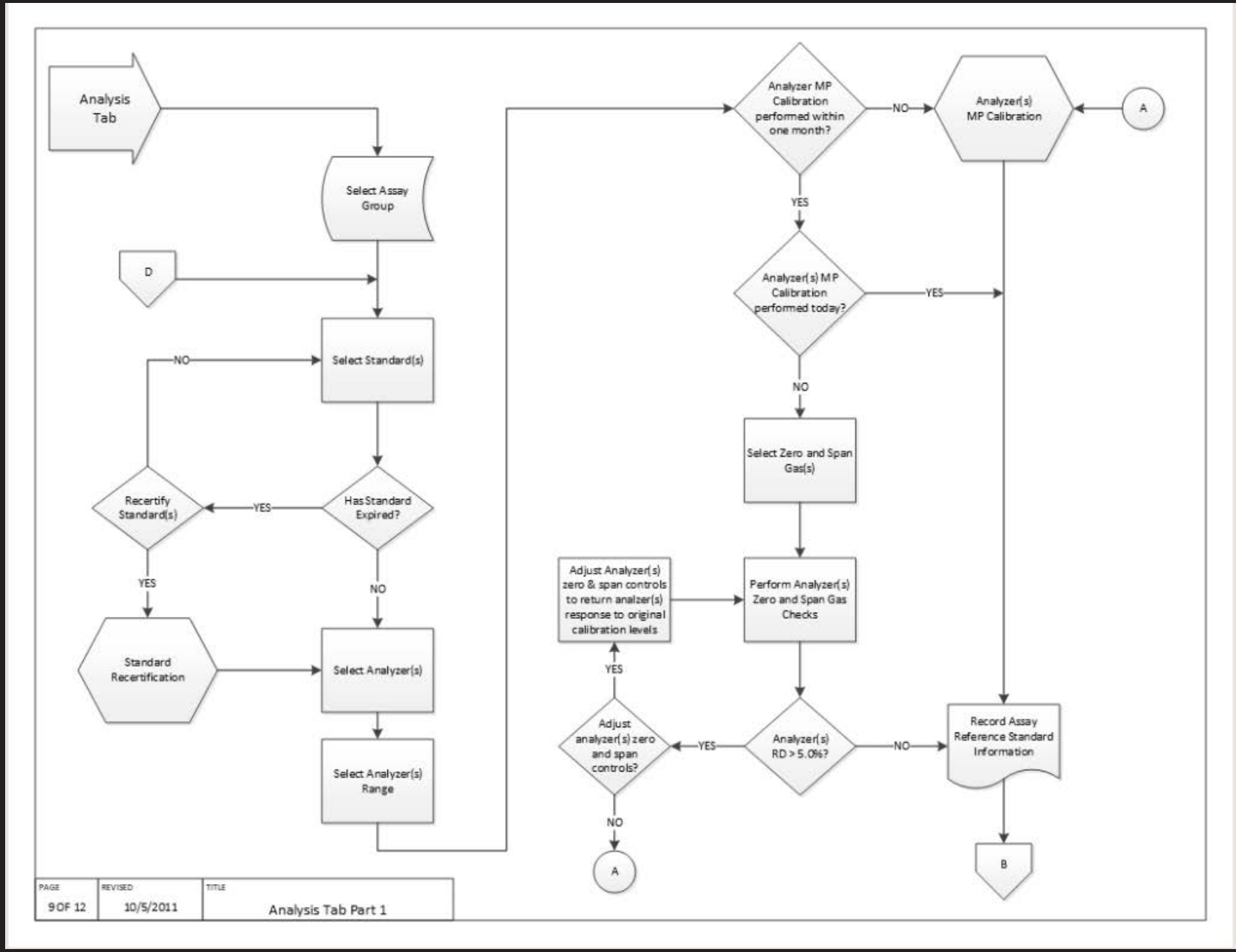
MULTIPOINT FLOW DIAGRAM



MULTIPOINT CALIBRATION CURVE



ASSAY FLOW DIAGRAM



ASSAY RESULTS

In this sheet the results of two or three Assays are entered. Calibration dates are entered so Assays having the same calibration uncertainty may treated correctly. (Assays having a common calibration share the same calibration uncertainty.)

Enter the results for up to three separate assays in chronological order below.

ASSAY 1

29.6437 = estimated concentration
0.52% = Expanded uncertainty (expressed as percentage of estimated concentration)
0.27 = portion of expanded uncertainty^2 due to calibration
3 = number of measurements
2/13/2023 = date of prior calibration

ASSAY 2

29.9759 = estimated concentration
0.39% = Expanded uncertainty (expressed as percentage of estimated concentration)
0.28 = portion of expanded uncertainty^2 due to calibration
3 = number of measurements
3/1/2023 = date of prior calibration

ASSAY 3 (if applicable)

29.9629 = estimated concentration
0.46% = Expanded uncertainty (expressed as percentage of estimated concentration)
1.00 = portion of expanded uncertainty^2 due to calibration
3 = number of measurements
3/1/2023 = date of prior calibration

Number of different calibrations represented by the above data:
N = 2 (If this value seems to be incorrect, check the dates entered for the three assays. The earliest data should be for Assay 1. Trailing spaces may cause N's formula to interpret identical dates as different.)

COMPARISONS

Assay 1 vs Assay 2

Calibration	Assay	Lower Confidence	Upper Confidence	Two One-Sided Equivalence with Assay 1: Lower Test Signficance	Two One-Sided Equivalence with Assay 1: Upper Test Signficance	Variance Components: Calibration	Variance Components: Imprecision	Total
1	1			----------	----------	0.0063888	0.017106	0.0234948
2	2	0.2132921	0.4512181	TRUE	FALSE	0.0039172	0.0099554	0.0138726

"FALSE" indicates an inconsistency where the observed confidence interval of the difference is beyond the tolerance level.

Assay 1 vs Assay 3

Calibration	Assay	Lower Confidence	Upper Confidence	Two One-Sided Equivalence with Assay 1: Lower Test Signficance	Two One-Sided Equivalence with Assay 1: Upper Test Signficance	Variance Components: Calibration	Variance Components: Imprecision	Total
1	1			----------	----------	0.0063888	0.017106	0.0234948
2	3	0.1927886	0.445546	TRUE	FALSE	0.0186746	1.868E-06	0.0186765

"FALSE" indicates an inconsistency where the observed confidence interval of the difference is beyond the tolerance level.
Nothing will appear here if no data have been entered for Assay 3.

Assay 2 vs Assay 3

Calibration	Assay	Lower Confidence	Upper Confidence	Two One-Sided Equivalence with Assay 1: Lower Test Signficance	Two One-Sided Equivalence with Assay 1: Upper Test Signficance	Variance Components: Calibration	Variance Components: Imprecision	Total
2	2			----------	----------	0.0039172	0.0099554	0.0138726
2	3	-0.124116	0.0979408	TRUE	TRUE	0.0186746	1.868E-06	0.0186765

"FALSE" indicates an inconsistency where the observed confidence interval of the difference is beyond the tolerance level.
Nothing will appear here if no data have been entered for Assay 3.

OVERALL ESTIMATE

Case = 15 (right click to see comment)

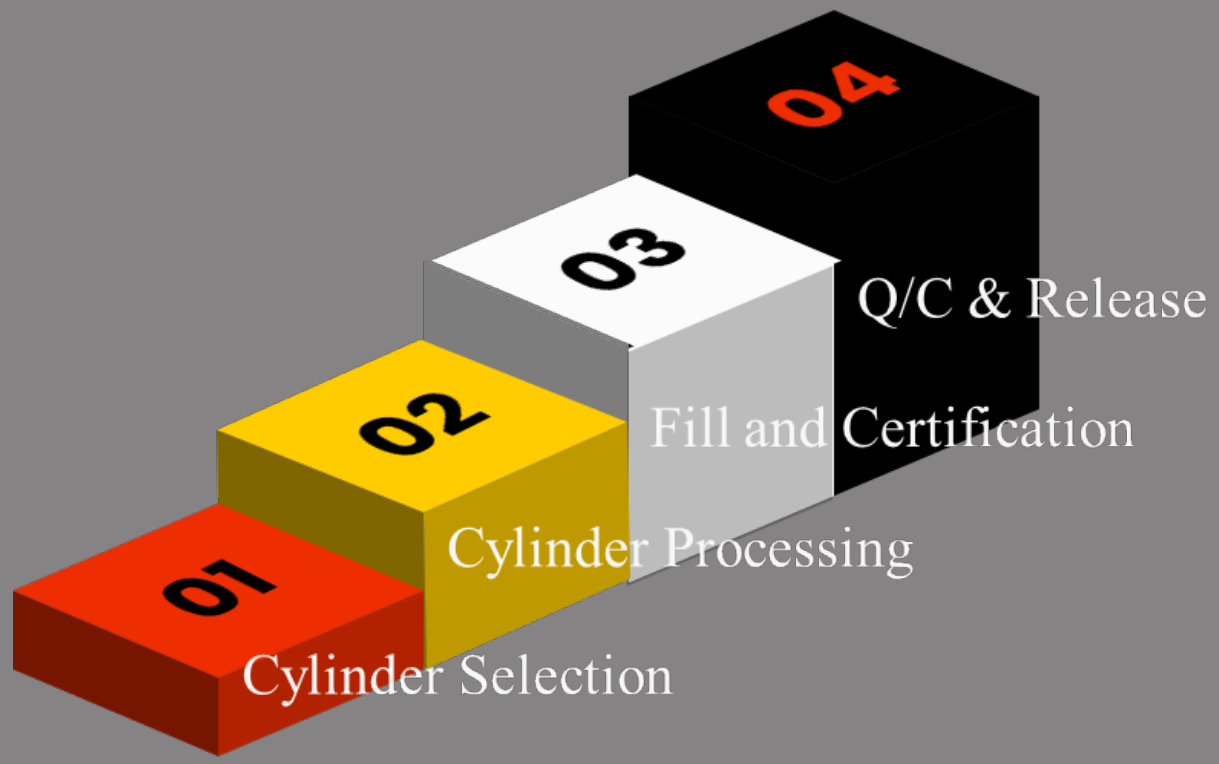
The standard error of the estimate produced in an assay is equal to approximately 1/2 of the "95% uncertainty." The inverse of the square of the standard error is the (raw) weighting factor used in producing an overall estimate of the concentration. The raw weights are adjusted (Adj. Wt.) so their sum is 1.00.

Calibration	Estimate	Exp. Uncert.	Raw Wt.	Adj. Wt.	Wt.*Conc.	Variance of Wt.*Est.
1	29.643695	0.517%	37401.80627	0.320	9.487	0.00241
2	29.962864	0.355%	79464.42242	0.680	20.374	0.00522
			0	0.000	0.000	0.00000

29.8607174 = overall estimate of the candidate standard's concentration
0.087 = Expanded uncertainty (concentration units)
0.293% = Expanded relative uncertainty

CYLINDER PROGRESSION STEPS

Full Process in View



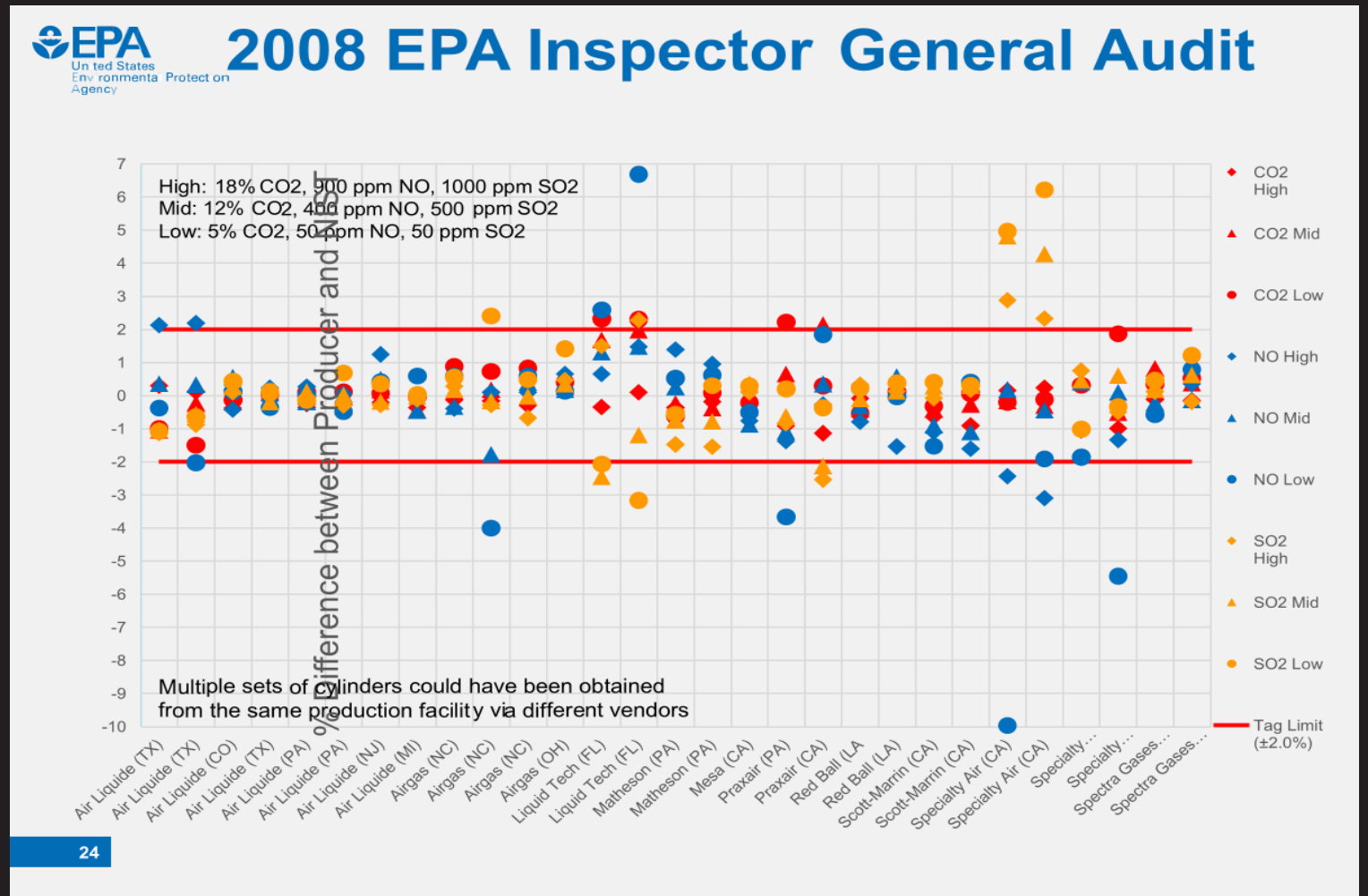
Q/C & Release
Review & Release.

Fill and Certification
Fill & Analyzation.

Cylinder Processing
Bake Out & Evacuation, Passivation Treatment and Pickling.

Cylinder Selection
Select appropriate cylinder and valve type.

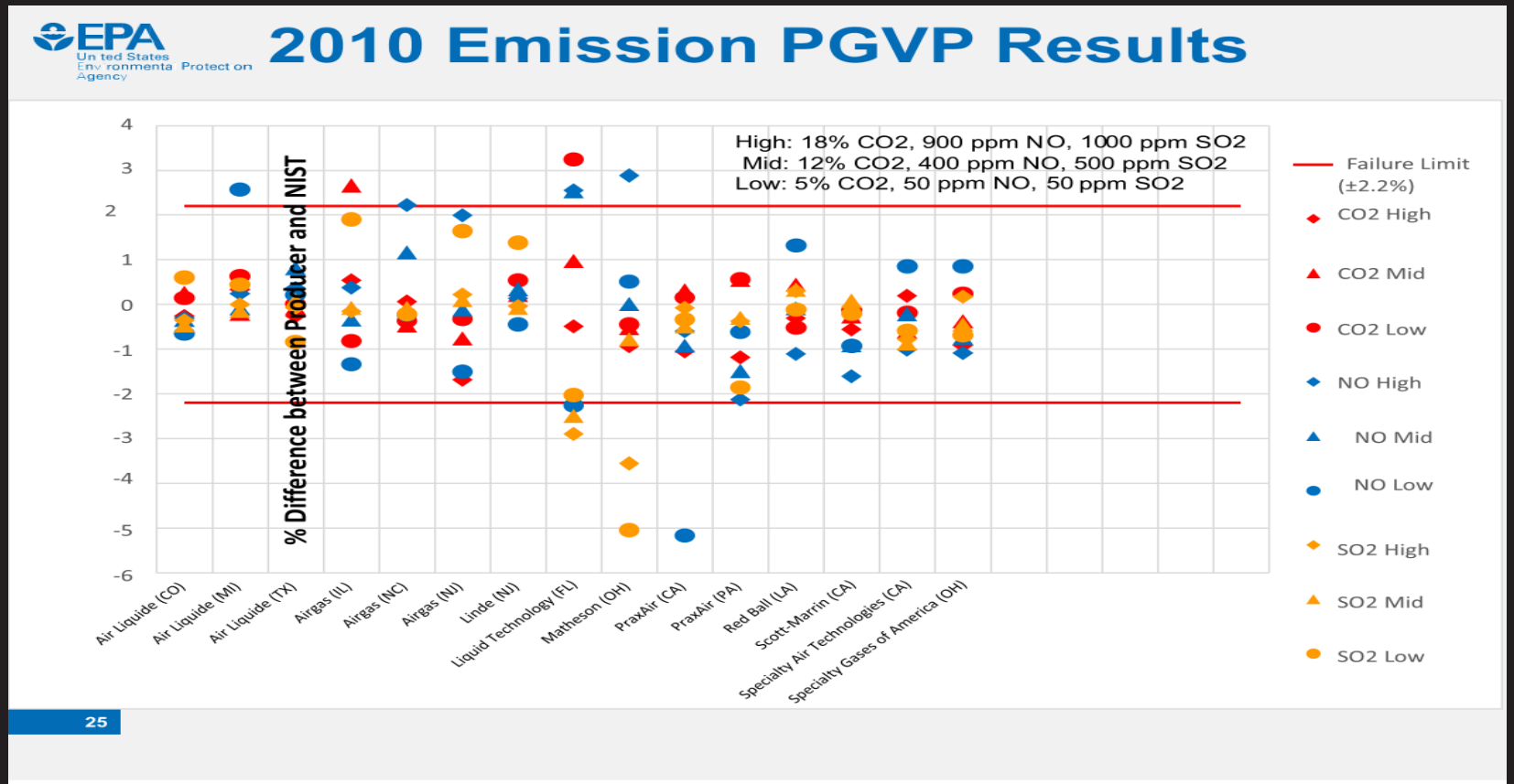
2008 EPA IG Audit



There were 261 components audited with 28 failures.

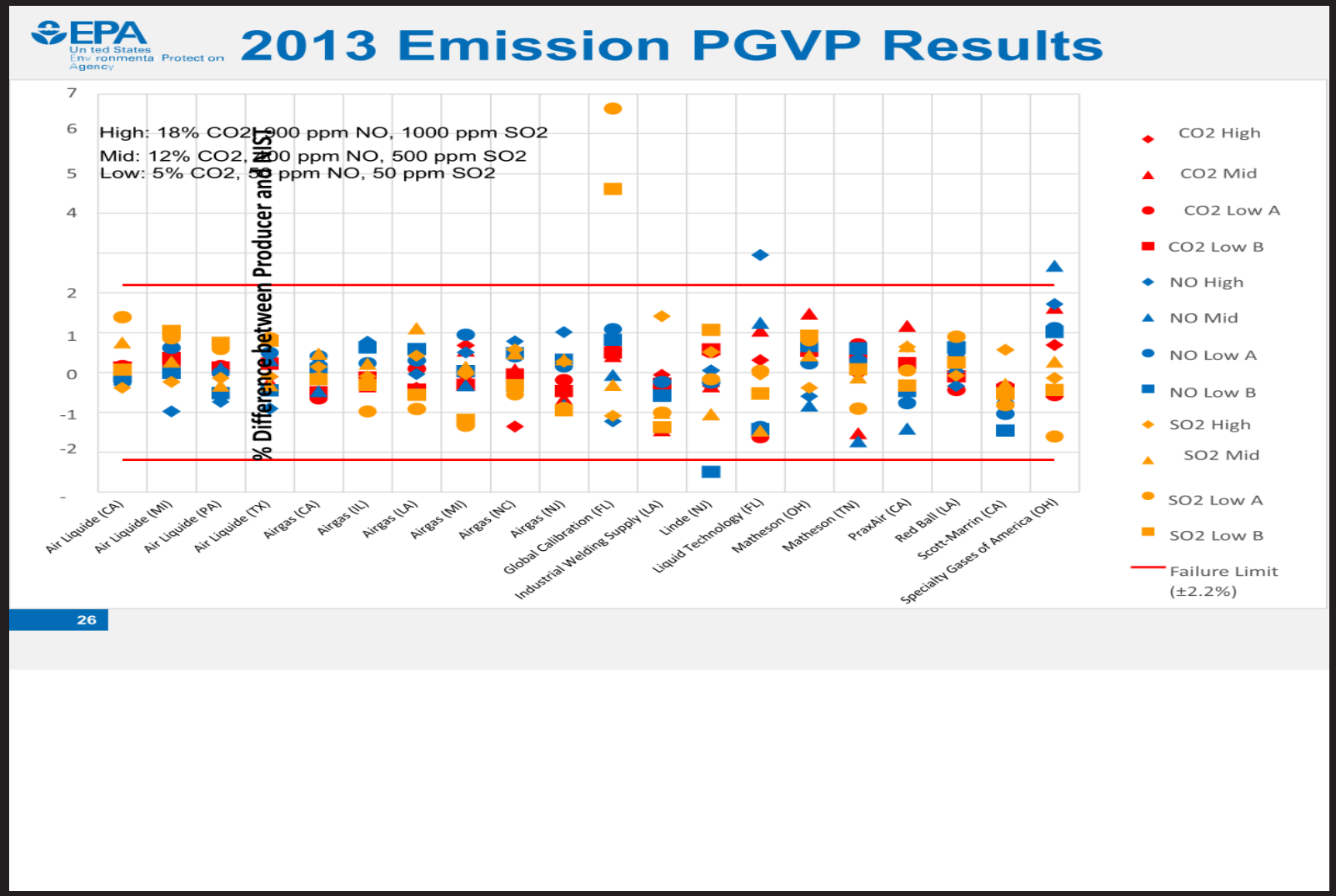
Total Failure Rate of 11%

2010 AUDIT RESULTS



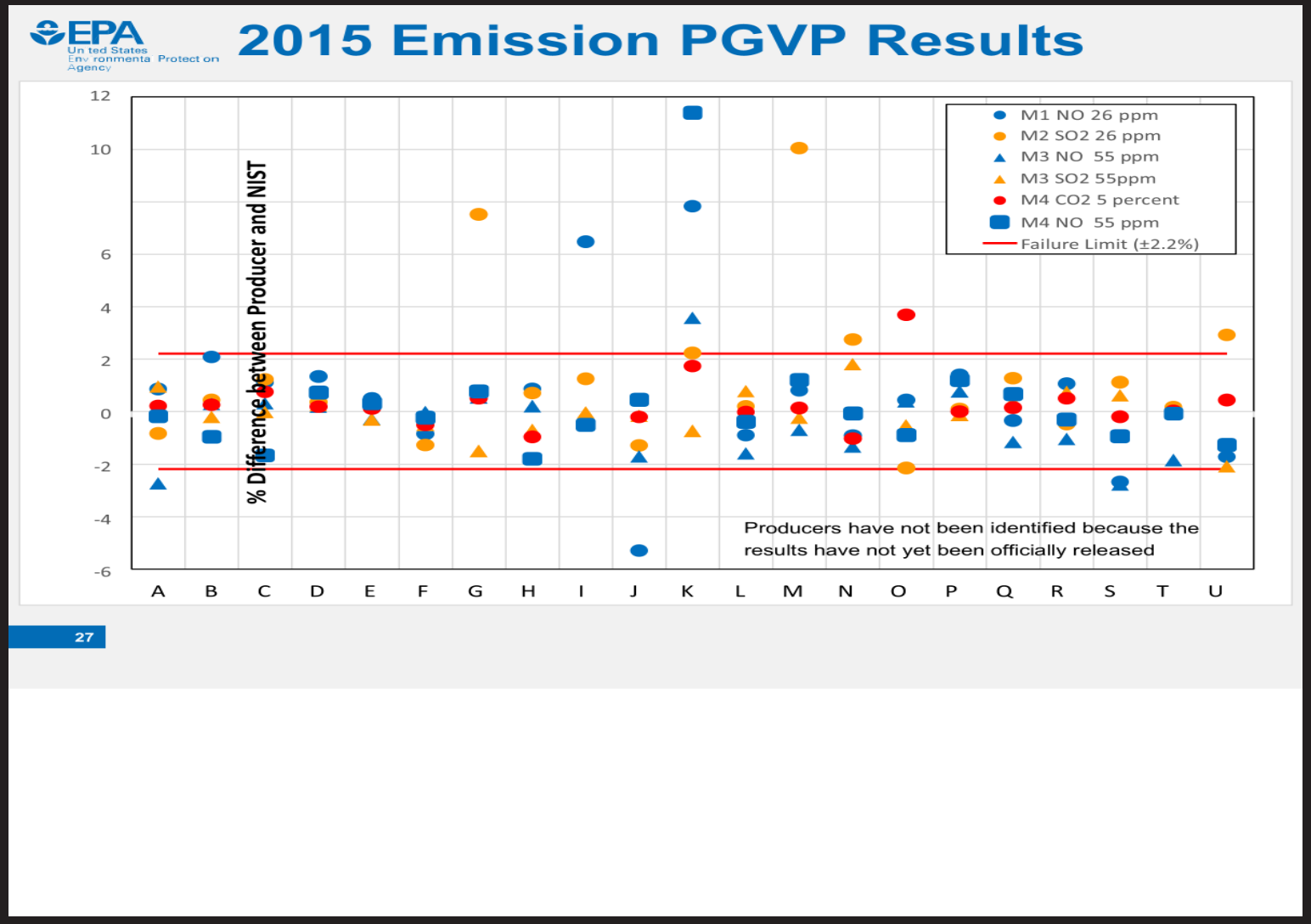
The results of the 2010 audit are generally consistent with previous audits- a 10% failure rate over all components analyzed, with 40% of the production sites failing at least one gaseous component

2013 LATEST AUDIT RESULTS



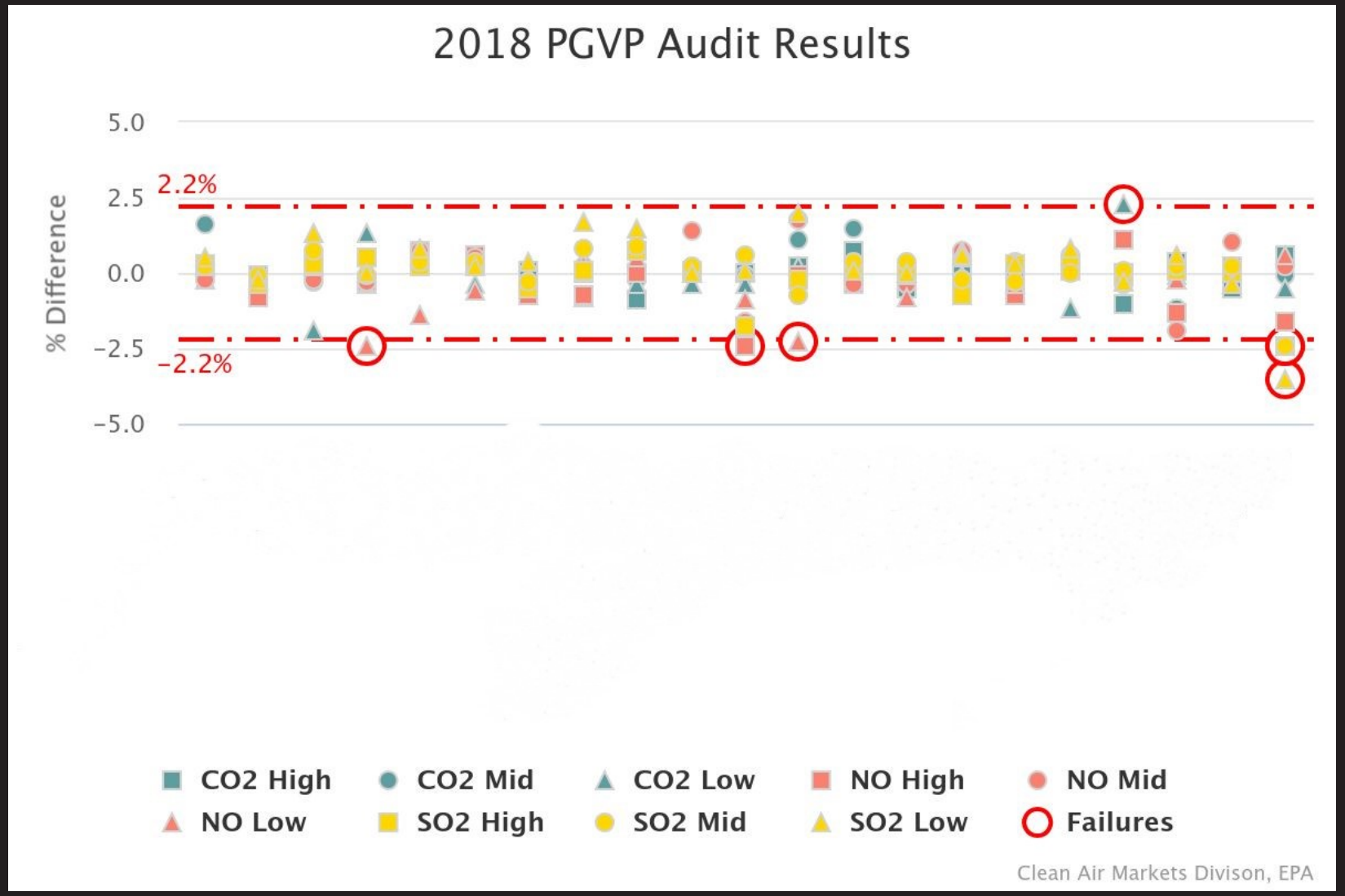
There were 3 producer who failed and 4 components.

2015 LATEST AUDIT RESULTS



There was another 11% failure rate. Worst Audit Result to date.

2018 LATEST AUDIT RESULTS



There were 66 cylinders audited with 6 failures.

Total Failure Rate of 9.1%

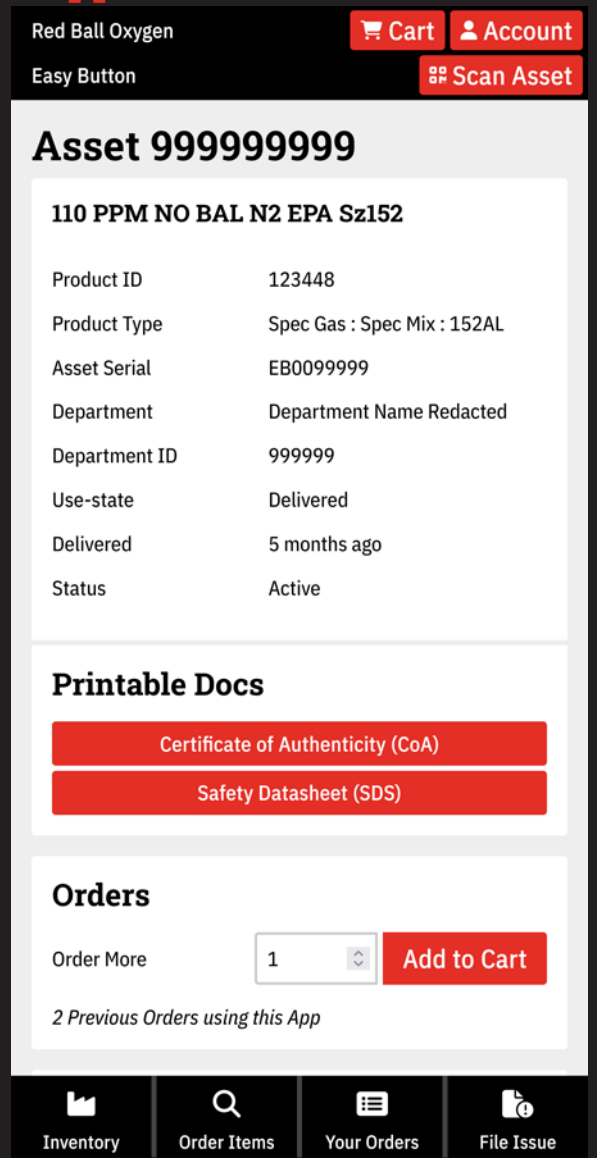
OBSTACLES IN CALIBRATION GAS MANUFACTURING

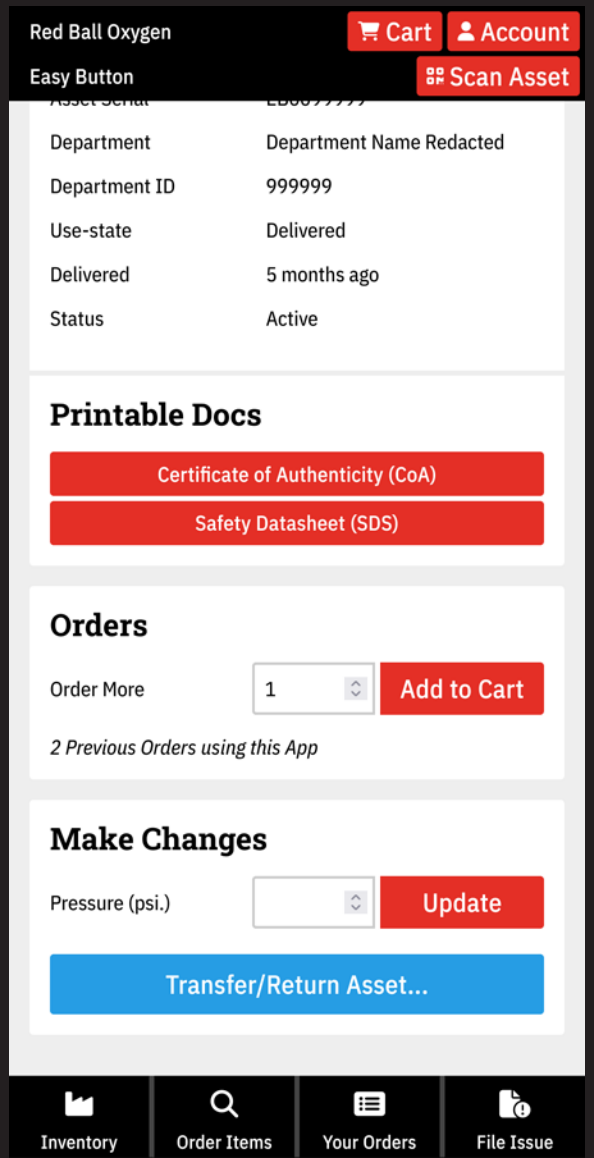
- Precise gas mixture creation challenges
- Managing instrument variability and sensor drift
- Adapting to regulatory changes and updates (NOx certification vs NIST traceability)
- Limited availability of NIST SRMs and equivalents
- Balancing cost and time efficiency in production
- High demand vs. production scalability issues

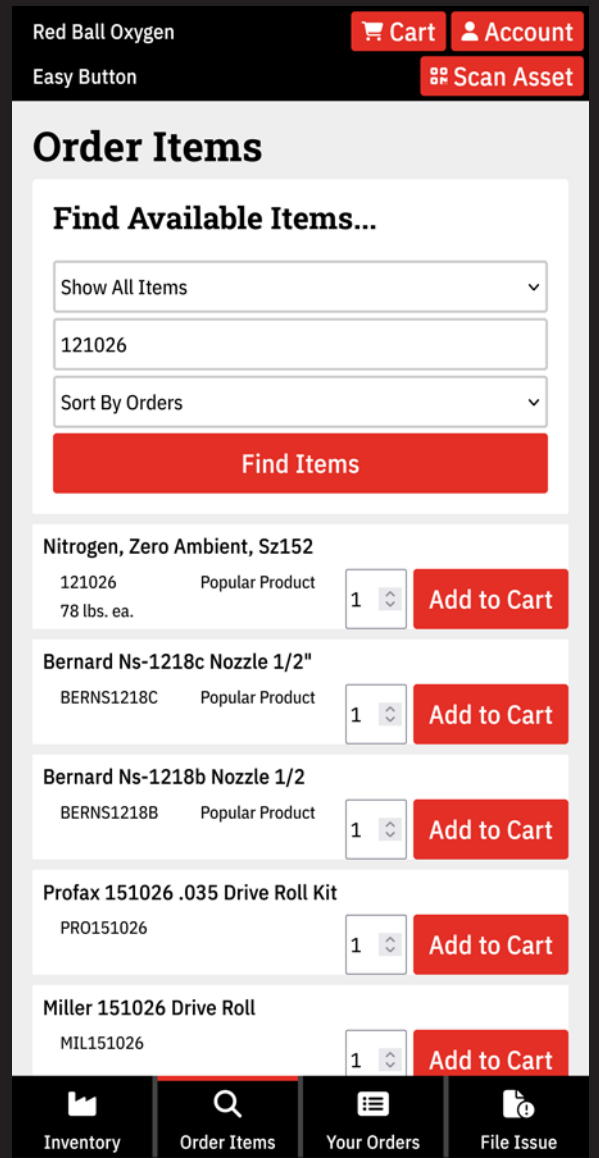
SRMs AVAILABLE

Gas	Concentration	UOM	Available
CO2/N2	0.5	%	Yes
CO2/N2	1	%	Yes
CO2/N2	1.5	%	Yes
CO2/N2	2	%	Yes
CO2/N2	7	%	Yes
CO2/N2	16	%	Yes
CO2/N2	3	%	No
CO2/N2	3.5	%	No
CO2/N2	500	PPM	No
CO/N2	25	PPM	Yes
CO/N2	50	PPM	Yes
CO/N2	500	PPM	Yes
CO/N2	1000	PPM	Yes
CO/Air	20	PPM	No
CO/Air	45	PPM	No
CO/N2	13	PPM	No
CO/N2	10	PPM	No
CO/N2	25	PPM	No
CO/N2	250	PPM	No
CO/N2	2500	PPM	No
CO/N2			No
CO/N2	5000	PPM	No
CO/N2	1000	PPM	No
CO/N2	1	%	No
CO/N2	2	%	No
CO/N2	4	%	No
CO/N2	8	%	No
Methane/Air	1	PPM	No
Methane/Air	10	PPM	No
Methane/Air	50	PPM	No
Methane/Air	100	PPM	No
NO/N2	1000	PPM	Yes
NO/N2	5	PPM	No
NO/N2	10	PPM	No
NO/N2	20	PPM	No
NO/N2	50	PPM	No
NO/N2	250	PPM	No
NO/N2	500	PPM	No
NO/N2	800	PPM	No
NO/N2	1500	PPM	No
NO/N2	3000	PPM	No
NO2/Air	100	PPM	No
O2/N2	2	%	Yes
O2/N2	10	%	Yes
O2/N2	21	%	Yes
SO2/N2	100	PPM	Yes
SO2/N2	500	PPM	Yes
SO2/N2	1000	PPM	Yes
SO2/N2	1500	PPM	Yes
SO2/N2	3500	PPM	Yes
SO2/N2	5	PPM	No
SO2/N2	50	PPM	No
SO2/N2	2500	PPM	No
Propane/Air	10	PPM	Yes
Propane/Air	50	PPM	Yes
Propane/Air	2500	PPM	Yes
Propane/Air	0.25	PPM	No
Propane/Air	3	PPM	No
Propane/Air	100	PPM	No
Propane/Air	250	PPM	No
Propane/Air	500	PPM	No

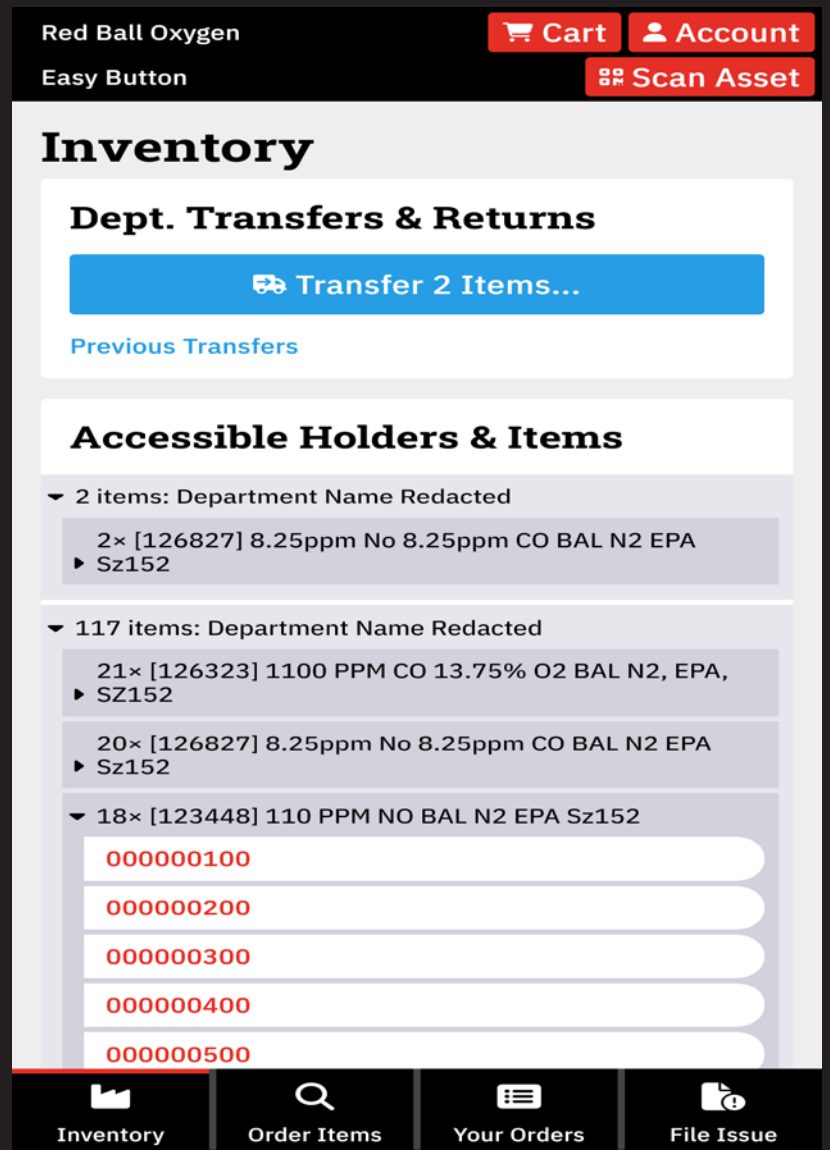
EZ BUTTON APP

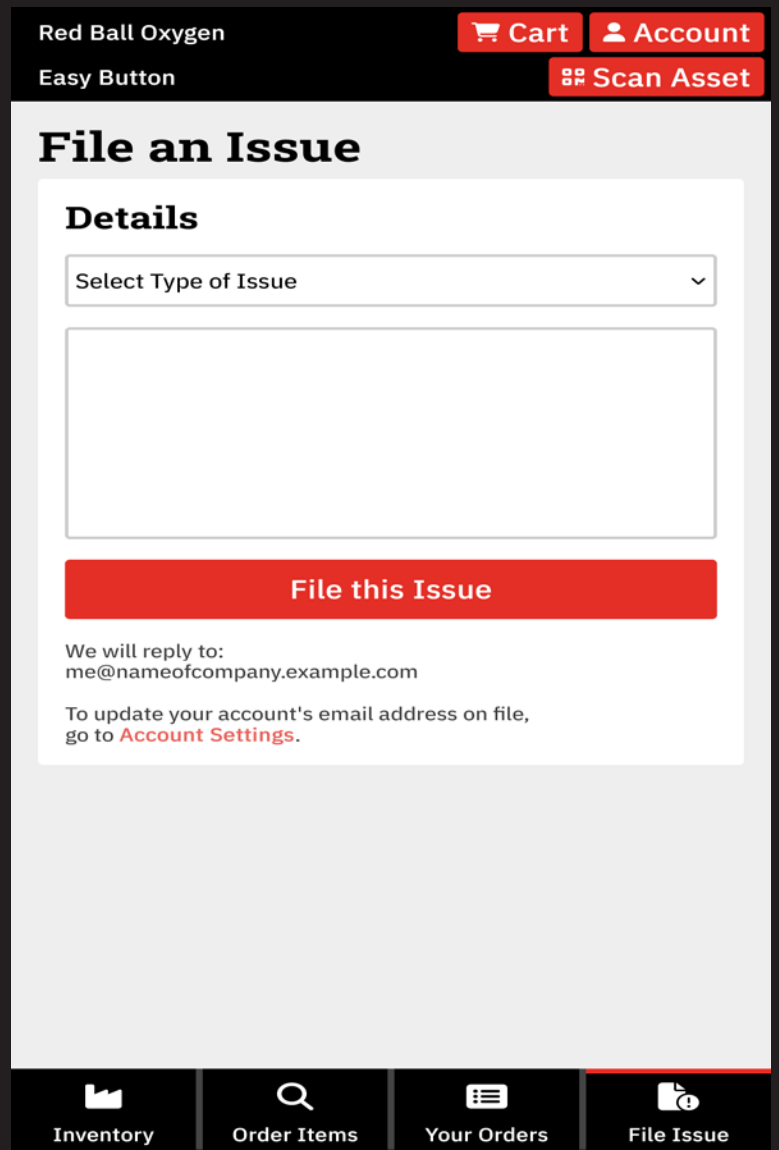






Continued


Red Ball Oxygen
Cart
Account
Easy Button
Scan Asset
Inventory
Dept. Transfers & Returns
Transfer 2 Items...
Previous Transfers
Accessible Holders & Items
2 items: Department Name Redacted
2× [126827] 8.25ppm No 8.25ppm CO BAL N2 EPA Sz152
117 items: Department Name Redacted
21× [126323] 1100 PPM CO 13.75% O2 BAL N2, EPA, SZ152
20× [126827] 8.25ppm No 8.25ppm CO BAL N2 EPA Sz152
18× [123448] 110 PPM NO BAL N2 EPA Sz152
000000100
000000200
000000300
000000400
000000500
Inventory
Order Items
Your Orders
File Issue


Red Ball Oxygen
Cart
Account
Easy Button
Scan Asset
File an Issue
Details
Select Type of Issue
File this Issue
We will reply to:
me@nameofcompany.example.com
To update your account's email address on file,
go to Account Settings.
Inventory
Order Items
Your Orders
File Issue

Last Step, Choose Wisely!

RED Ball
TGS

RED BALL
TECHNICAL GAS SERVICES

FINAL QUESTION WE SHOULD ASK

Is the process paving the way toward the success we envision?

MARK PATTEN

RED BALL
TECHNICAL GAS SERVICES