

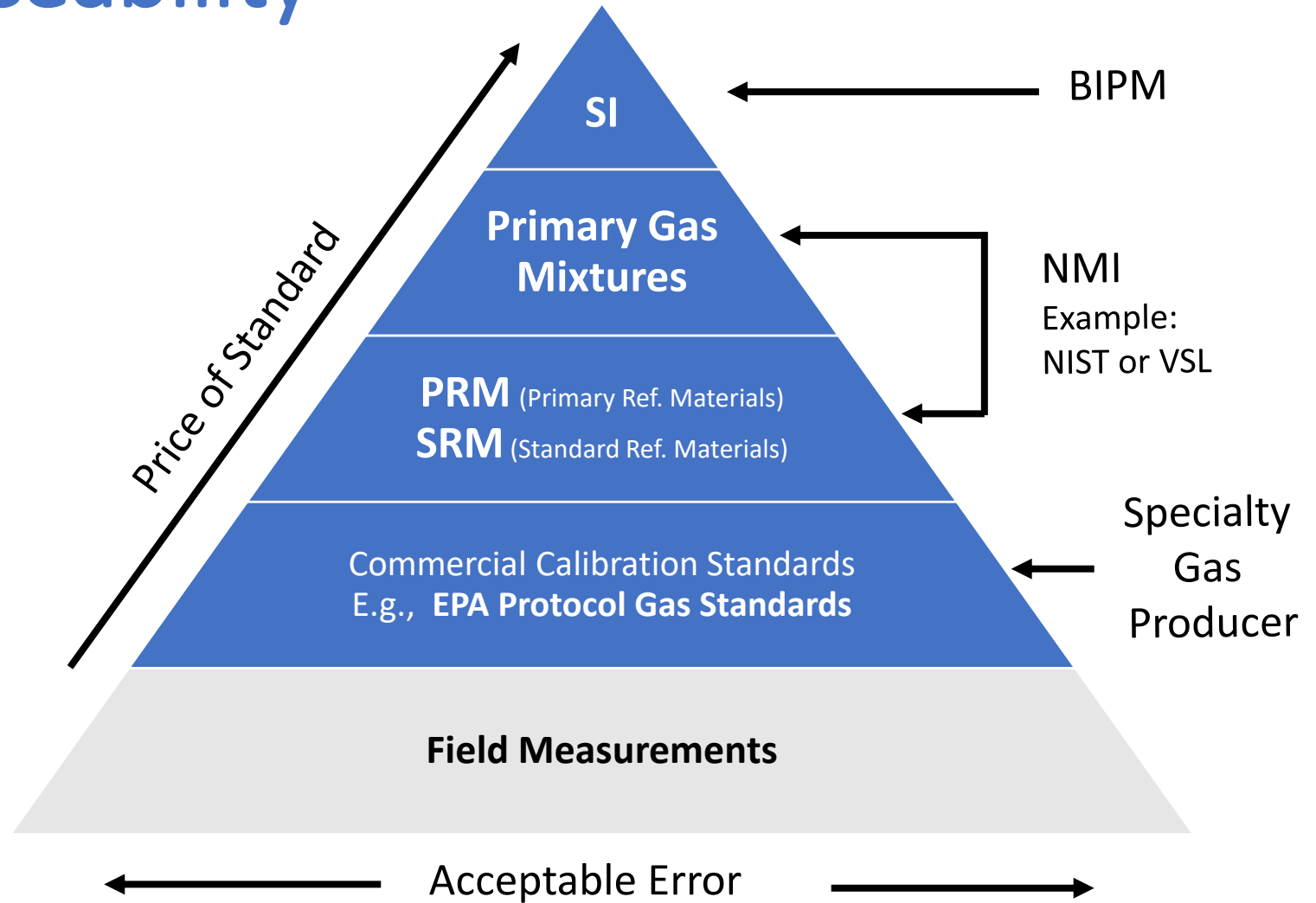


# EPA Protocol Gas and Ambient Air Protocol Gas Verification Program

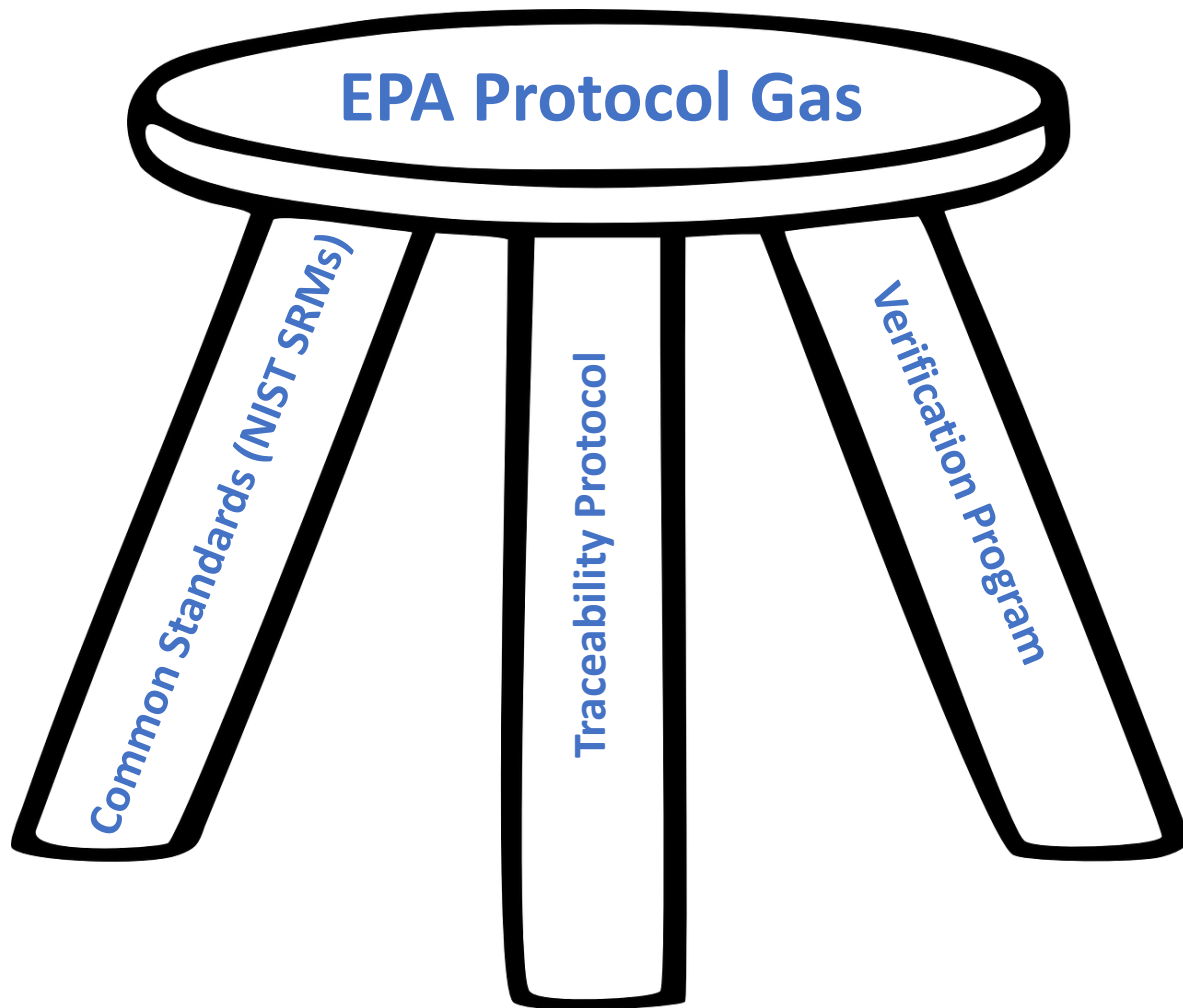
Doug Jager  
EPA OAQPS  
Ambient Air Monitoring Group

# Metrological Traceability

**Metrological Traceability:** property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.



# Components of the EPA Protocol Gas Program



## The Verification Program:

- is a critical component of the EPA Protocol Gas Program

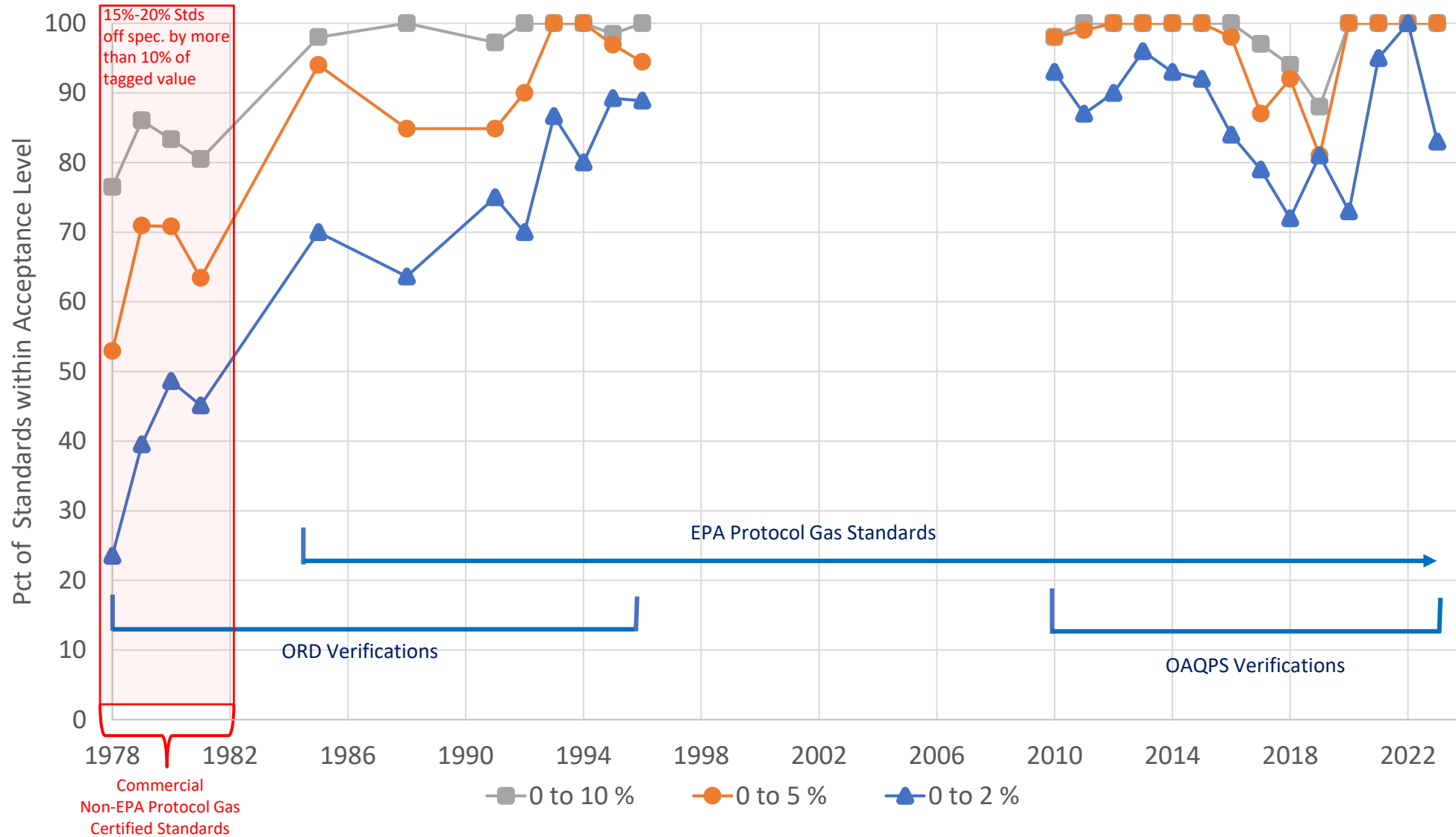
## Verification Program Hurdles:

- Readily Accessible NIST SRMs and VSL PRMs for EPA
- More Cylinders needed from SLTs for verification
  - *Shipping Cylinders is a pain*
- Better Understanding of which Protocol Gas Producers are used in the SLT monitoring networks
  - Will use new AQS Cylinder Tracking features to resolve this issue ← *More on this later in Presentation*

## Reminder:

- CO, SO<sub>2</sub>, and NO<sub>2</sub>, Calibration Standards for Ambient Air Monitoring are required to be EPA Protocol Gas Standards
  - These calibration standards cannot just be Certified NIST Traceable Standards for NAAQS monitoring

# Percentage of Gas Standards (within Given Accuracy Range)

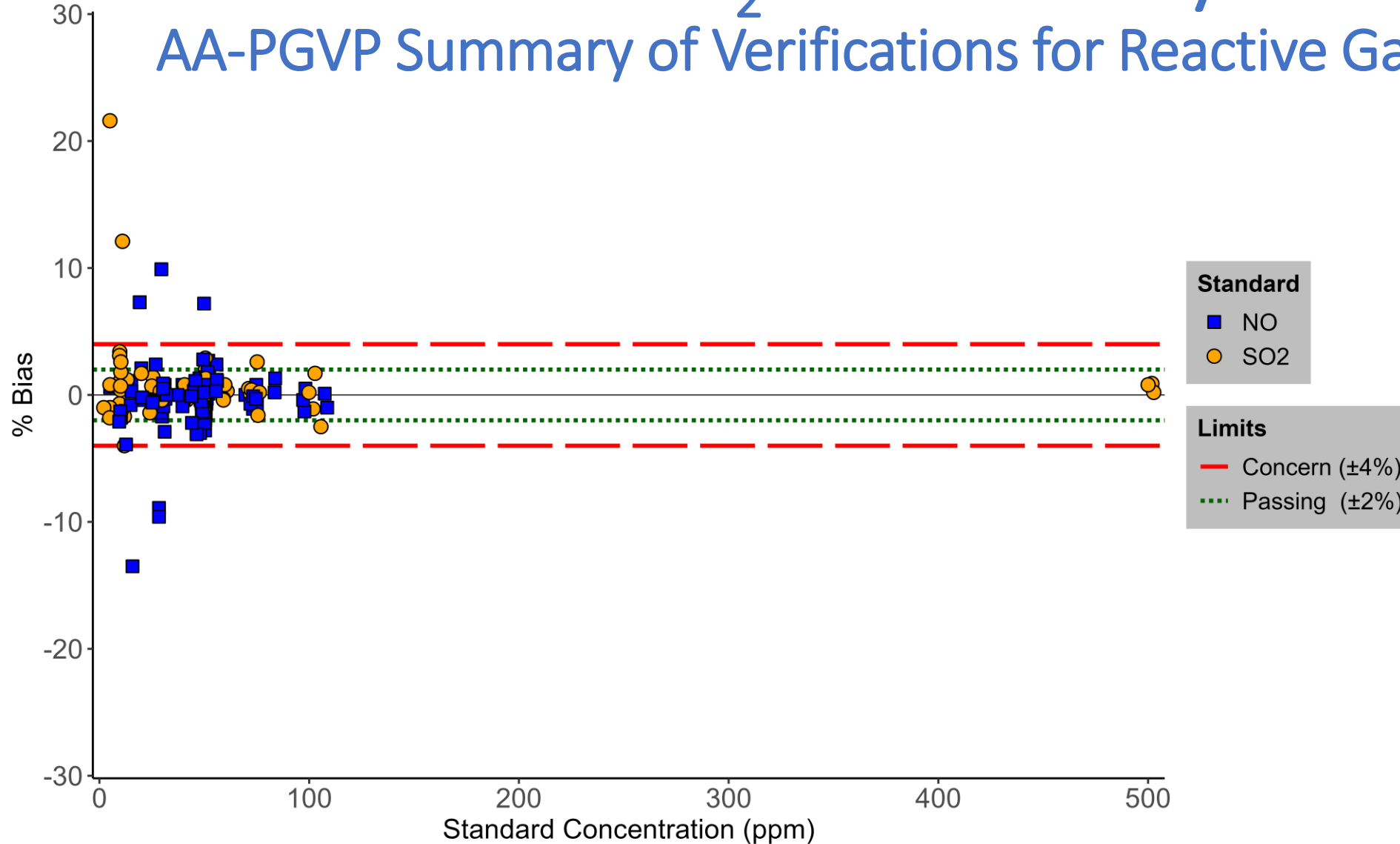


## Milestones:

- **1970:** Clean Air Act
- **1972:** NIST Compressed Gas SRMs
- **1978:** EPA Traceability Protocol (2012 is current rev.)
- **1985:** EPA Protocol Gas Standards
- **1996-2010:** Hiatus in Verification Prog.
- **2010-2018:** EPA OAP Verifications occur about every 3-yrs (*not shown in Fig*)
- **2010 – present:** EPA OAQPS Verifications quarterly

# Bias in NO and SO<sub>2</sub> Standards by Concentration

## AA-PGVP Summary of Verifications for Reactive Gas Standards



### Summary of Figure:

Of all the cylinders verified by OAQPS, EPA's assayed concentrations for Protocol Gas Cylinder Standards generally have been within  $\pm 2\%$  of their certified concentrations.

Cylinders with the highest biases are those cylinders certified at lower concentrations ( $\leq 20$  ppm)

# Reminder: NO<sub>2</sub> Stability Concerns

- EURAMET study in 2021 ([Metrology for Nitrogen Dioxide](#)) determined NO<sub>2</sub> standards from National Metrology Institutes (NMI) vary in quality and often are not stable
- OAQPS 2/25/2022 Memo:  
[EPA Protocol Gas Long-Term Stability Requirements](#)
  - Clarifies that NO<sub>2</sub> is not an EPA Protocol Gas Standard for ambient air monitoring until further notice
- Insufficient stability data for EPA to establish a maximum certification period in the EPA Traceability Protocol for NO<sub>2</sub>
- NIST SRMs are not available for NO<sub>2</sub>
- Absence of EPA Oversight and Verification of these Standards:
  - NPAP does not assess performance of Direct Read NO<sub>2</sub> FEMs
  - OAQPS AA-PGVP lacks equipment and standards needed for performing verification assays of NO<sub>2</sub> cylinders
  - OAP PGVP (our emissions counterpart to ambient) has never verified NO<sub>2</sub> standards as part of their verification program
- EPA is working to revise the Traceability Protocol to establish testing and assay procedures for reactive gas standards like NO<sub>2</sub>

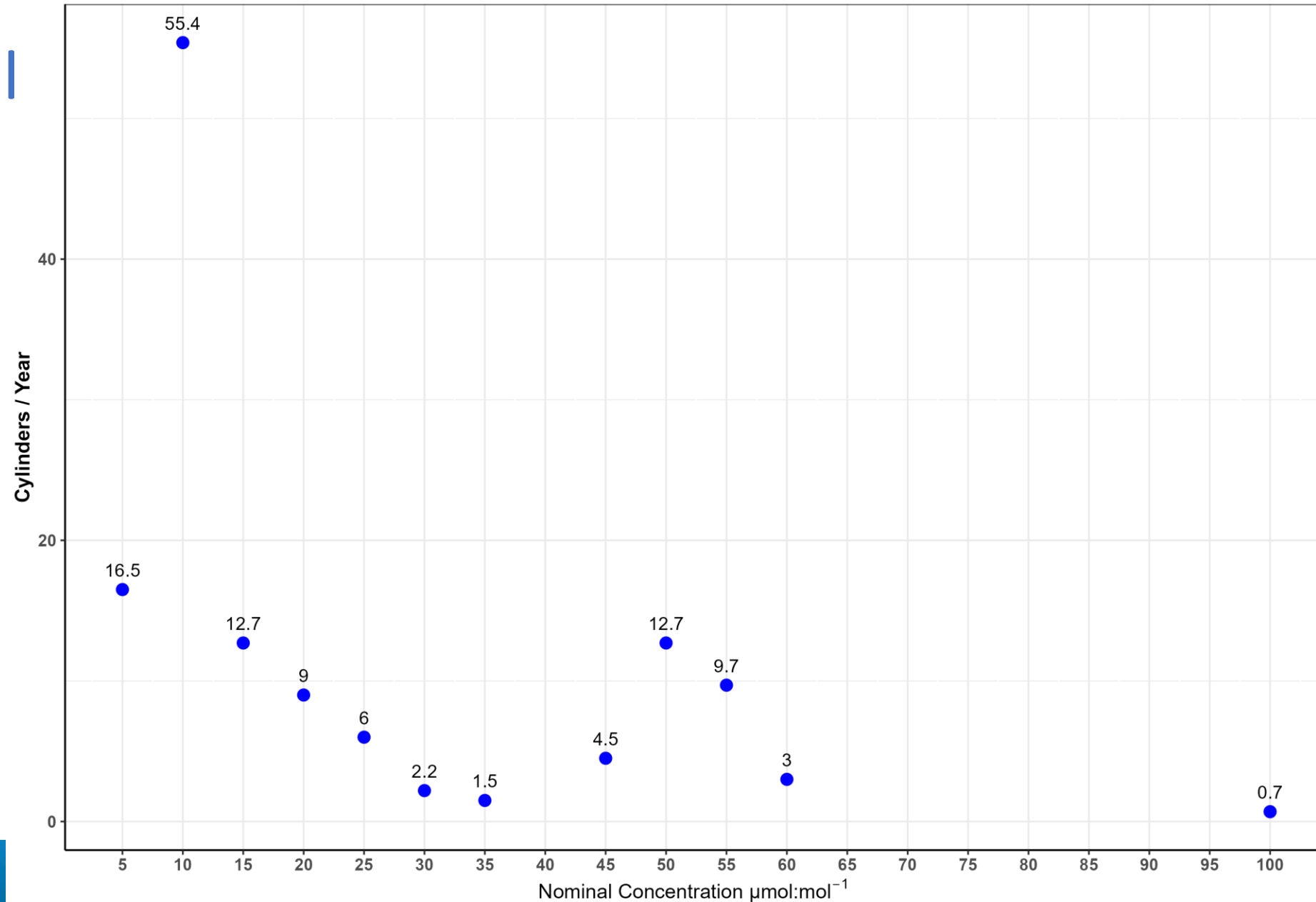
# Sulfur Dioxide (SO<sub>2</sub>) EPA Protocol Gas Standards

Ambient Air Program's Annual Calibration Standard Usage

## Estimated Annual Sulfur Dioxide EPA Protocol Gas Cylinder Usage

Cylinder Distribution based on SLT submissions using AQS Maintain Cylinder Form

Note: only 30% of agencies have entered cylinders using the Maintain Cylinder Form



Cylinders assumed lifetime is 3 years. Standards required to have Relative Uncertainty < ±2%, k=2.  
Data aggregated at binwidth = 5 µmol/mol and estimated by normalizing national network size to distribution of cylinder concentrations entered in AQS.



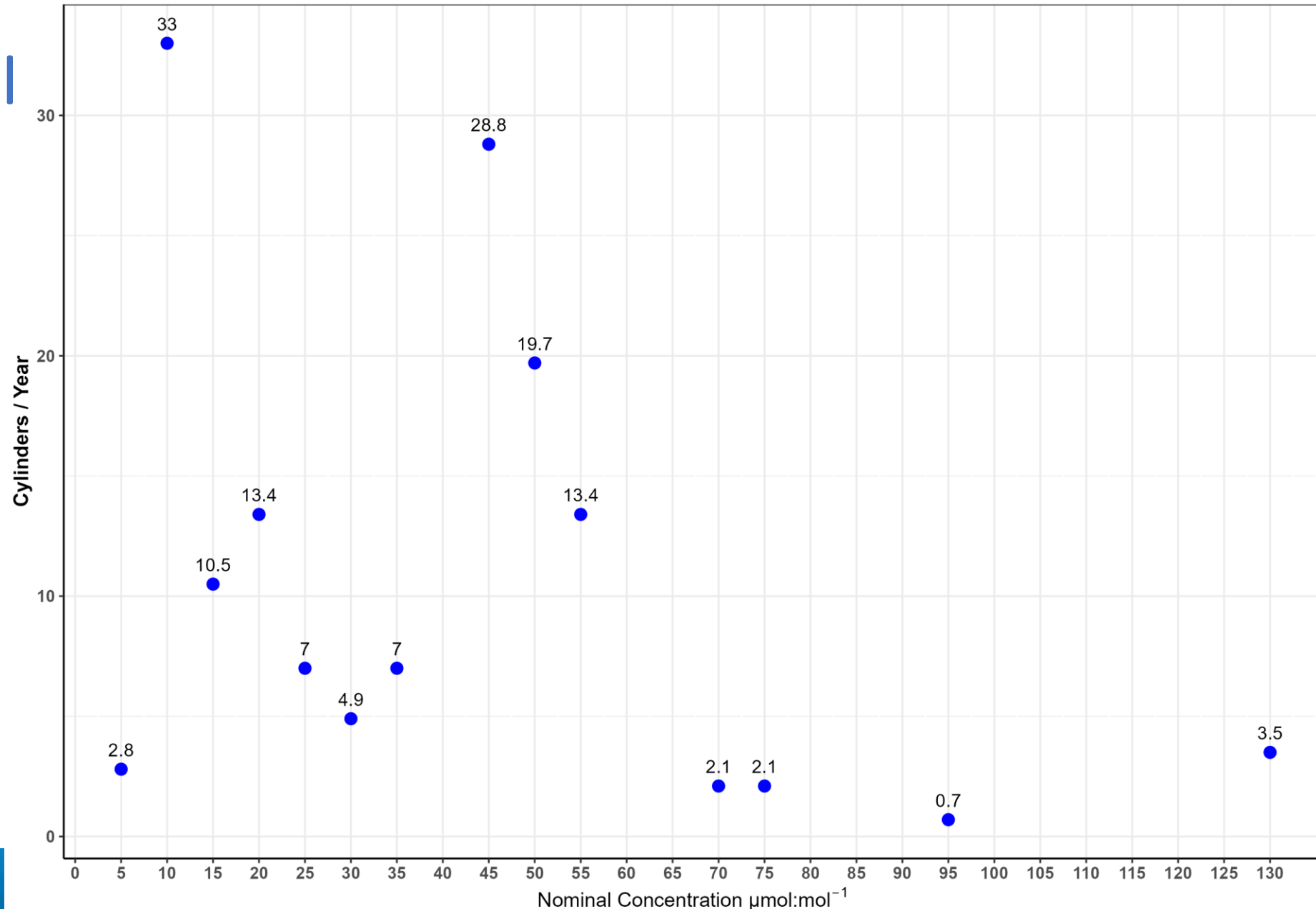
# Nitric Oxide (NO) EPA Protocol Gas Standards

Ambient Air Program's Annual Calibration Standard Usage

## Estimated Annual Nitrogen Oxide EPA Protocol Gas Cylinder Usage

Cylinder Distribution based on SLT submissions using AQS Maintain Cylinder Form

Note: only 30% of agencies have entered cylinders using the Maintain Cylinder



Cylinders assumed lifetime is 3 years. Standards required to have Relative Uncertainty  $< \pm 2\%$ ,  $k=2$ .  
Data aggregated at binwidth =  $5 \mu\text{mol}/\text{mol}$  and estimated by normalizing national network size to distribution of cylinder concentrations entered in AQS.





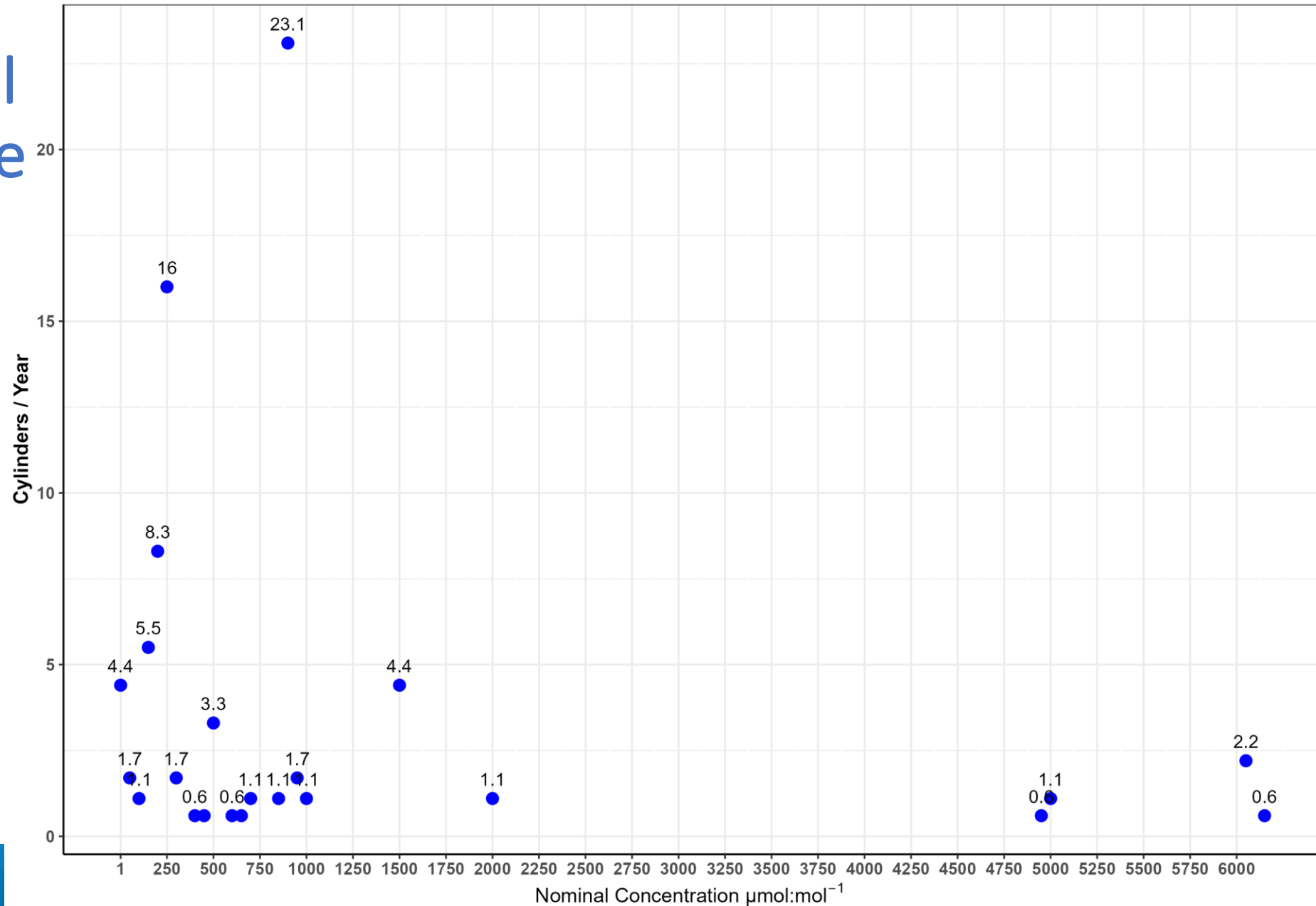
# Carbon Monoxide (CO) EPA Protocol Gas Standards

Ambient Air Program's Annual Calibration Standard Usage

## Estimated Annual Carbon Monoxide EPA Protocol Gas Cylinder Usage

Cylinder Distribution based on SLT submissions using AQS Maintain Cylinder Form

Note: only 30% of agencies have entered cylinders using the Maintain Cylinder



Cylinders assumed lifetime is 3 years. Standards required to have Relative Uncertainty < ±2%, k=2.  
Data aggregated at binwidth = 50 µmol/mol and estimated by normalizing national network size to distribution of cylinder concentrations entered in AQS.



# Understanding which Protocol Gas Producers are Used in the SLT Monitoring Networks

## Gas Calibration Standards

An effective tracking system is lacking for documenting the cylinder standards used for calibrating analyzers in the ambient air monitoring program.

### This has impacted:

- **AA-PGVP:** AA-PGVP's ability to identify which SLTs should be requested to provide cylinders for verification per Part 58 App. A §2.6.1.2.
- **Standard Validity:** EPA's ability to ensure that only QA/QC check results obtained by using valid calibration standards (non-expired standards) are loaded to AQS.
- **EPA Protocol Gas:** EPA's ability to proactively enforce regulatory requirements that calibrations and QA/QC checks of ambient air CO, SO<sub>2</sub>, and NO<sub>2</sub> analyzers are only performed with standards certified as EPA Protocol Gas.

# Development of the Solution:

## Leverage AQS to Document Compressed Gas Calibration Standards

OAQPS over the past 3 years has developed an AQS solution to track and document the calibration cylinder standards used in the ambient air monitoring networks.

These features are developed and currently deployed in AQS as 'optional use'. Currently, SLTs can opt to not use these new AQS cylinder tracking features.

First announced to monitoring community during the 2022 NAAMC.

## Adoption Rate of AQS Cylinder Tracking Features by SLTs

Between 2023-2024:

- 30% of SLTs have used the AQS Maintain Cylinder Form for at least 1 Cylinder.
- 12% of SLTs have documented the cylinder used for their CO, SO<sub>2</sub>, or NO<sub>2</sub> QA/QC results.

## Feedback Received

Many RO's, SLT's and a commercial DAS vendor have informed OAQPS that they will not begin using and supporting these new AQS features until a 'required use' date is established by EPA.

# AQS Cylinder Tracking Features Required Starting July 1, 2025

## Next Phase of Implementation (End of Optional Use Period)

- SLTs required to report to AQS the cylinders used to generate QA/QC test atmospheres for CO, SO<sub>2</sub>, and NO<sub>2</sub> analyzers.
- The cylinder metadata reporting is achieved by requiring that QA/QC checks loaded to AQS must include the cylinder used for the check.
- “Required Use” date for this transition will begin **July 1, 2025**.
  - Date provides SLTs a further year of planning to implement the AQS QA/QC requirement.
  - Date allows for 2024 Data Certifications (due May 1, 2025) to not be impacted by the change
- EPA will evaluate SLT’s rates for successfully including cylinders on QA-Transactions through July 1, 2025. Based on this review and feedback received from SLTs during this period EPA may choose to extend the Optional Use Period past July 2025.

# Required Cylinder Tracking Starting July 1, 2025 (Benefits vs Costs)

## Benefits

- Process leverages existing AQS QA/QC data submittal processes
- OAQPS will be able to identify SLTs that should be requested to provide cylinders to the AA-PGVP for verification.
- Creates database rules that ensure only QA/QC check results obtained from valid calibration standards are loaded to AQS.
- AQS will automatically ensure that QA/QC checks of ambient air CO, SO<sub>2</sub>, and NO<sub>2</sub> analyzers are only performed with EPA Protocol Gas Standards.
- The AA-PGVP Annual Survey System will no longer be needed.
- Savings in contract dollars that are no longer needed to support AA-PGVP Annual Survey System.

## Costs

- Beginning July 2025:
  - QA/QC checks for CO, SO<sub>2</sub>, and NO<sub>2</sub> that do not have cylinders associated will not load to AQS
- Beginning May 2026:
  - The AMP-600 Certification Report will highlight those monitors from CY-2025 that lack adequate QA/QC checks reported to AQS during the annual data certification.

# AQS Guidance

[www.epa.gov/aqs](http://www.epa.gov/aqs)



## AQS –Documentation

- All Manuals and Guides

- AQS User Guide; see “Maintain QA” for guidance on the Maintain forms
- AQS Transaction Formats includes guidance on adding the PGVP-ID and Cylinder ID
  - QA – 1-Point QC
  - QA – Annual PE

- AQS Code List

- Cylinder Producers (list of valid PGVP-IDs for EPA Protocol Gas Producers)
- Cylinders (list of all cylinders entered by SLTs into AQS)

# AQS Guidance

## Maintain Cylinder Form

- Form Starts in 'Query Mode'
- User must first cancel out of Query Mode to begin entering parameters into Cylinder.
- Form is operating in Data Entry Mode and not Query Mode when the 'Cancel Query' Button is Grayed Out. **See icon circled in Red.**
- Remember to click the save button "Floppy Disk Icon" in upper left of application to save cylinder.

The screenshot displays the 'Maintain Cylinder' form in the AQS application. The top toolbar contains various icons, with the floppy disk icon (representing 'Cancel Query') circled in red. The form fields are as follows:

- PGVP Id: [Dropdown]
- Cylinder Id: [Text Field]
- Owning Agency: 1108 [Dropdown] | US EPA/OAQPS [Text Field]
- Certification Date (YYYYMMDD): [Text Field]
- Expiration Date (YYYYMMDD): [Text Field]
- Comments: [Text Field]

Parameter Code	Unit Code	Certified Concentration
[Dropdown]	[Dropdown]	[Text Field]
[Dropdown]	[Dropdown]	[Text Field]
[Dropdown]	[Dropdown]	[Text Field]
[Dropdown]	[Dropdown]	[Text Field]
[Dropdown]	[Dropdown]	[Text Field]

FRM-40353: Query cancelled.  
Record: 1/1 | List of Values

# AQS Guidance

## Example of QA-Transaction File for 1-Point QC checks submitted by SLTs

QA		1-Point QC		0053		04		007		0011		42401		1		20230320		1		100		008		76.86		76				
QA		1-Point QC		0053		04		007		0011		42401		1		20230403		1		100		008		76.87		76				
QA		1-Point QC		0053		04		007		0011		42401		1		20230417		1		100		008		78.84		76				
QA		1-Point QC		0053		04		007		0011		42401		1		20230501		1		100		008		76.11		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230515		1		100		008		78.23		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230526		1		100		008		75.45		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230612		1		100		008		75.18		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230626		1		100		008		73.40		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230710		1		100		008		75.01		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230713		1		100		008		73.32		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230724		1		100		008		75.04		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230807		1		100		008		75.12		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230808		1		100		008		76.90		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230821		1		100		008		75.71		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230901		1		100		008		77.22		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230905		1		100		008		73.88		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20230918		1		100		008		75.98		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231002		1		100		008		73.32		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231003		1		100		008		74.42		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231012		1		100		008		73.69		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231026		1		100		008		74.33		76		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231109		1		100		008		76.22		75		D6		SX61898
QA		1-Point QC		0053		04		007		0011		42401		1		20231122		1		100		008		74.26		76		D6		SX61898

SLTs will not be able to leave the last 2 fields blank for CO, SO<sub>2</sub>, and NO<sub>2</sub> after **July 1, 2025**.

**PGVP-ID** and **Cylinder-ID** of cylinder appended to end of transaction string

**PGVP-ID** used for identifying EPA Protocol Gas Producer.

**Cylinder-ID** links cylinder to a site/monitor and makes process 'auditable' in AQS. Allows for validating certification period of standard to assessment date of the QC check.



# Certificate of Analysis (COA) showing fields needed on AQS Maintain Cylinder Form

Praxair Distribution, Inc.  
 5700 S. Alameda Street  
 Los Angeles CA 90058  
 Tel: 323-585-2154  
 Fax: 714-542-6689  
 PGVP ID: **F22018**

Praxair Distribution, Inc.  
 5700 S. Alameda Street  
 Los Angeles CA 90058  
 Tel: 323-585-2154  
 Fax: 714-542-6689  
 PGVP ID: **F22018**

**SIS / EPA PROTOCOL GAS**

DocNumber: [Redacted]  
 Customer & [Redacted]

PRAXAIR PROSPEC BARE BOTTLE  
 6880 S 2300 E  
 SALT LAKE CITY UT 84121

Fill Date: 11/07/2018  
 Lot Number: 70775599  
 Part Number: NI SD100E-AQ

Fill Date: 10/26/2018  
 Lot Number: 70086829904  
 Cylinder Style & Outlet: AQ CGA 660  
 Cylinder Pressure and Volume: 2200 psig 84 ft3

**For this Certificate enter PGVP ID = "F2" On the AQS Maintain Cylinder Form**

Certified Concentration		
Expiration Date:	11/07/2026	NIST Traceable
Cylinder Number:	LL23589	Expanded Uncertainty
99.9 ppm	Sulfur dioxide	± 1 %
Balance	Nitrogen	



**Certification Information:** Certification Date: 11/07/2018 Term: 96 Months Expiration Date: 11/07/2026

This cylinder was certified according to the 2012 EPA Traceability Protocol, Document #EPA-600/R-12/531, using Procedure G1. Do Not Use this Standard if Pressure is less than 100 PSIG.

**Analytical Data:** (R=Reference Standard, Z=Zero Gas, C=Gas Candidate)

1. Component: Sulfur dioxide

Requested Concentration: 100 ppm  
 Certified Concentration: 99.9 ppm  
 Instrument Used: Horiba VIA-510, 5203551011  
 Analytical Method: NDIR  
 Last Multipoint Calibration: 10/14/2018

First Analysis Data:				Date			
Z:	0	R:	95.2	C:	100.3	Conc:	100.3
R:	95.2	Z:	0	C:	100.4	Conc:	100.4
Z:	0	C:	100.2	R:	95.1	Conc:	100.2
UOM:	ppm	Mean Test Assay:	100.3	ppm			

Reference Standard: Type / Cylinder #: NTRM / SA16843  
 Concentration / Uncertainty: 95.17 ppm ±1%  
 Expiration Date: 03/30/2020

Traceable to: SRM # / Sample # / Cylinder #: NTRM#SA16843 / 120702 / NTRM#SA16843  
 SRM Concentration / Uncertainty: 95.17 PPM / ±1.00 PPM  
 SRM Expiration Date: 03/30/2020

Second Analysis Data:				Date			
Z:	0	R:	95.2	C:	99.4	Conc:	99.3
R:	95.2	Z:	0	C:	99.6	Conc:	99.5
Z:	0	C:	99.8	R:	95.3	Conc:	99.7
UOM:	ppm	Mean Test Assay:	99.5	ppm			

Analyzed By: Quinn Hailes

Certified By: Leeanna Flores



# Questions?