

2023 Overview of EPA Protocol Gases

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Outline of Presentation

- Basic concepts in gas metrology
- Regulatory requirements for calibration gases
- Historical background of EPA protocol
- Reference standards for protocol assays
- Types of EPA Protocol Gases
- Audits of EPA Protocol Gases
- Status of NO₂ EPA Protocol Gases

NIST Definition of Traceability

- <https://www.nist.gov/calibrations/traceability>
- Metrological traceability is defined as the property of a measurement result whereby the result can be related to a **specific reference standard** through a documented **unbroken chain of calibrations** with each link contributing to the **overall measurement uncertainty**.
- NIST reference standard has an estimated uncertainty.
- Uncertainty propagates for each link in the chain.
- Statistical procedures for estimating the uncertainty.

Regulatory Air Pollution Monitoring

- Industries and governments are required to measure air pollution emissions and ambient air quality
- Measurements have legal and economic impacts
- Measurements are made by calibrated instruments
- Calibrations typically use compressed gas mixtures
- **Gas mixtures need to be accurate, stable, and trusted**

Rationale for EPA Protocol Gases

- In the early 1970s, commercially-produced certified standards were perceived as being **too inaccurate** and **too unstable** for use in calibration and audits of analyzers being used for regulatory monitoring
- Legal and economic impacts of calibration inaccuracy require the use of high-value, **accurate**, and **stable** calibration gases

1970 EPA Regulations to Control Air Pollution from Motor Vehicles

- Calibration gases for hydrocarbon (HC) and carbon monoxide (CO) analyzers: “The actual concentrations should be known to within **+/- 2 percent** of the true values.”

1973 EPA Regulations to Control Air Pollution from Aircraft Engines

- Calibration gases for HC, CO, and nitrogen oxides (NO_x) analyzers: “The actual concentrations should be known to within **+/- 2 percent** of the actual values.”

1993 EPA Regulations for Continuous Emission Monitoring under the Acid Rain Program

- Calibration gases include the following:
 - NIST Standard Reference Materials (SRMs);
 - NIST/EPA Certified Reference Materials (CRMs);
 - EPA Protocol Gases must be vendor-certified to be within **2.0 percent** of the concentration specified on the cylinder label (tag value).

EPA Methods for Monitoring Stationary Source Emissions and Ambient Air Quality

- Depending on the particular method, stationary source calibration and audit gases must be traceable either to a NIST gaseous SRM, to a NIST standard or to producer-certified standards
- Ambient air monitoring QA program requires that calibration gases be EPA Protocol Gases, but it does not have a specified acceptance criterion for the accuracy of these gas mixtures.

Origin of EPA Protocol Gases

- 1977 EPA-Industry Quality Control Symposium
- National Bureau of Standards (NBS), automotive industry, and specialty gas producers attended
- Scott Environmental Technology developed a draft protocol
- Protocol is a general analytical recipe, which may be used by any analyst with any analytical instrument
- Triplicate comparisons between a candidate standard and an analytical reference standard (e.g., NBS SRM)
- Monthly multipoint calibrations, daily zero and span checks
- Reactive gas stability checked 3 times over 60 days
- Certification period up to one year
- EPA Protocol Gases are certified and sold by producers

1978 EPA Traceability Protocol

- Anyone can use the protocol to assay gas mixtures
- Protocol No. 1 uses continuous emission monitors (CEMs) to assay gas mixtures without dilution
- Protocol No. 2 uses ambient air quality monitors to assay gas mixtures using gas dilution systems
- Triplicate comparisons between a candidate standard and an analytical reference standard (e.g., NBS SRM)
- Monthly multipoint calibrations, daily zero and span checks
- Reactive gases' stability checked 2 times over 7 days
- Reactive gases must be reanalyzed every six months
- No direct government oversight of or blanket certification of producers, but EPA will audit EPA Protocol Gases

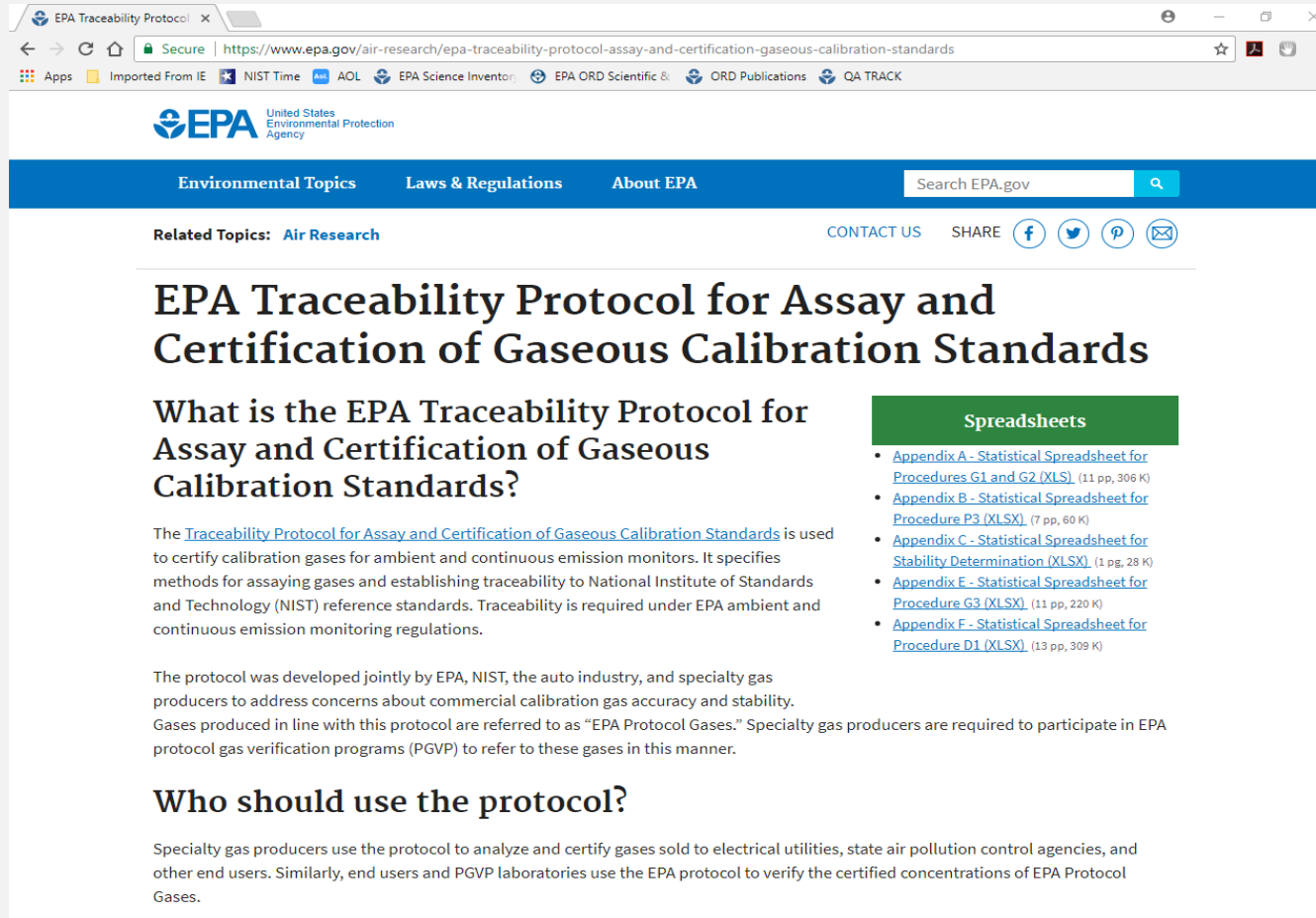
Analytical Reference Standards for Assay of EPA Protocol Gases

- NIST Standard Reference Material (SRM)
- NIST-Traceable Reference Material (NTRM)
- NIST Research Gas Material (RGM)
- VSL (Dutch) Primary Reference Material (PRM)
- NPL (UK) Primary Standard Reference Gas
- Gas Manufacturer's Intermediate Standard (GMIS),
which are assayed using NIST, VSL or NPL standards
- The **limited availability** of reference standards remains
the biggest obstacle to producing EPA Protocol Gases

Revisions to Protocol in 1987, 1993, 1997, and 2012

- Incremental changes to protocol over the years
- Longer certification periods
- More sophisticated statistical calculations to estimate uncertainty and stability
- New analytical procedures to assay permeation devices, gas dilution systems, and zero air materials

<https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards>



The screenshot shows a web browser window displaying the EPA Traceability Protocol webpage. The browser's address bar shows the URL: <https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards>. The page features the EPA logo and navigation links for Environmental Topics, Laws & Regulations, and About EPA. A search bar is present with the text "Search EPA.gov". Below the navigation bar, there is a "Related Topics" section with a link to "Air Research". The main heading of the page is "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards". Below this heading, there is a sub-heading "What is the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards?". The text explains that the protocol is used to certify calibration gases for ambient and continuous emission monitors. It specifies methods for assaying gases and establishing traceability to National Institute of Standards and Technology (NIST) reference standards. Traceability is required under EPA ambient and continuous emission monitoring regulations. The protocol was developed jointly by EPA, NIST, the auto industry, and specialty gas producers to address concerns about commercial calibration gas accuracy and stability. Gases produced in line with this protocol are referred to as "EPA Protocol Gases." Specialty gas producers are required to participate in EPA protocol gas verification programs (PGVP) to refer to these gases in this manner. A green box labeled "Spreadsheets" contains a list of links to various statistical spreadsheets: Appendix A - Statistical Spreadsheet for Procedures G1 and G2 (XLS) (11 pp, 306 K), Appendix B - Statistical Spreadsheet for Procedure P3 (XLSX) (7 pp, 60 K), Appendix C - Statistical Spreadsheet for Stability Determination (XLSX) (1 pg, 28 K), Appendix E - Statistical Spreadsheet for Procedure G3 (XLSX) (11 pp, 220 K), and Appendix F - Statistical Spreadsheet for Procedure D1 (XLSX) (13 pp, 309 K). Below the text, there is a section titled "Who should use the protocol?" which states that specialty gas producers use the protocol to analyze and certify gases sold to electrical utilities, state air pollution control agencies, and other end users. Similarly, end users and PGVP laboratories use the EPA protocol to verify the certified concentrations of EPA Protocol Gases.

Certification Periods

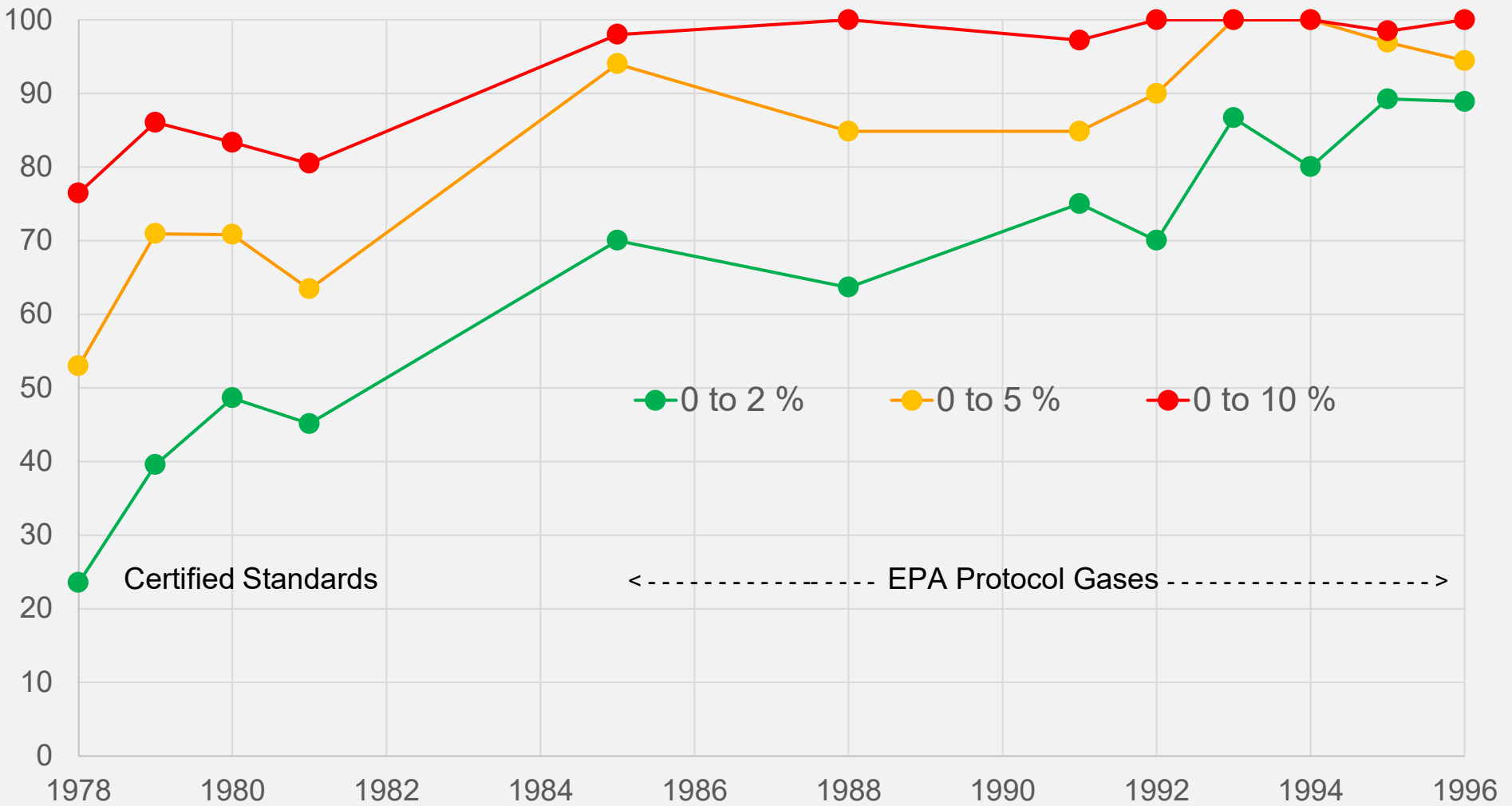
Maximum Certification Periods in Passivated Aluminum Cylinders

Components	Balance gas	Concentration range	Period (years)
Ambient VOCs	Nitrogen	1 ppb to 1 ppm	4
Ammonia	Nitrogen	5 to 50 ppm	2
Carbon dioxide	Air	100 to 500 ppm	8
Carbon dioxide	Nitrogen	10 ppm to 20%	8
Carbon monoxide	Air	1 ppm to 10%	8
Carbon monoxide	Nitrogen	1 ppm to 15%	8
Formaldehyde	Nitrogen	0.5 to 10 ppm	1
Hydrogen chloride	Nitrogen	10 to 5000 ppm	2
Hydrogen sulfide	Nitrogen	5 to 1000 ppm	3
Methane	Air	1 to 1000 ppm	8
Methanol or ethanol	Nitrogen or Air	75 to 500 ppm	4
Natural gas components	Natural gas	Contact NIST	8
Nitric oxide	O ₂ -free nitrogen	0.5 to 20 ppm	3
Nitric oxide	O ₂ -free nitrogen	20 ppm to 1%	8
Nitrogen dioxide	Nitrogen or Air	1 ppm to 1%	TBD
Nitrous oxide	Air	TBD by NIST	6
Oxides of nitrogen	Air	10 ppm to 1%	6
Oxygen	Nitrogen	10 ppm to 25%	8
Propane	Air	0.1 to 500 ppm	8
Propane	Nitrogen	100 ppm to 2%	8
Sulfur dioxide	Nitrogen	1 to 50 ppm	4
Sulfur dioxide	Nitrogen	50 ppm to 1%	8
Zero air material	Air	Not applicable	Unlimited
Multicomponent mixtures	—	—	See text
Mixtures with lower concentrations	—	—	See text

Audit Program for EPA Protocol Gases

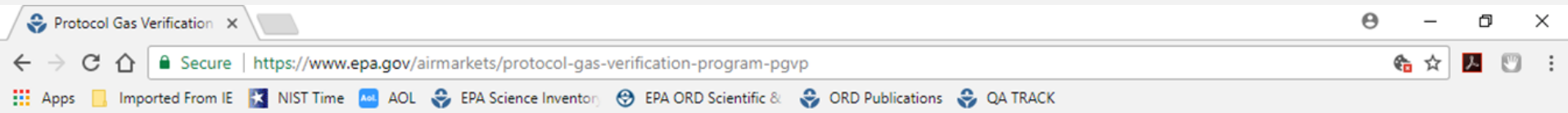
- 1978 protocol stated “EPA will initiate a **national performance audit program** of cylinder gas prepared by this protocol. Cylinder gas prepared following the protocol will be obtained directly or indirectly by EPA and analyzed in their laboratory for accuracy compared to the gas manufacturer's reported concentration.”
- Cylinders were purchased surreptitiously through a third-party buyer
- Assayed at an independent laboratory using NIST SRMs as standards
- Results and producers’ identities disseminated to public
- Results can be used to guide end users’ purchasing decisions
- Audits of commercial certified standards from 1978 through 1981
- Audits of EPA Protocol Gases from 1985 through 1996, then hiatus until 2008 audit by EPA Office of Inspector General

Percentage of Audited Cylinder Gases within a Given Accuracy Range






Protocol Gas Verification Program (PGVP)

- EPA Office of Inspector General audited EPA Protocol Gases in 2008 and recommended restarting audit program
- Only PGVP participants and their distributors can sell EPA Protocol Gases
- Emissions PGVP purchased cylinders from producers by third-party buyer with assay by NIST
- Ambient air PGVP obtained cylinders from agencies or producers with assay by EPA regional labs
- PGVP results and producers' names disseminated to public
- PGVP results can be used to guide end users' purchasing decisions



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Protocol Gas Verification Program (PGVP)

Participants

Reporting Instructions

Audit Results

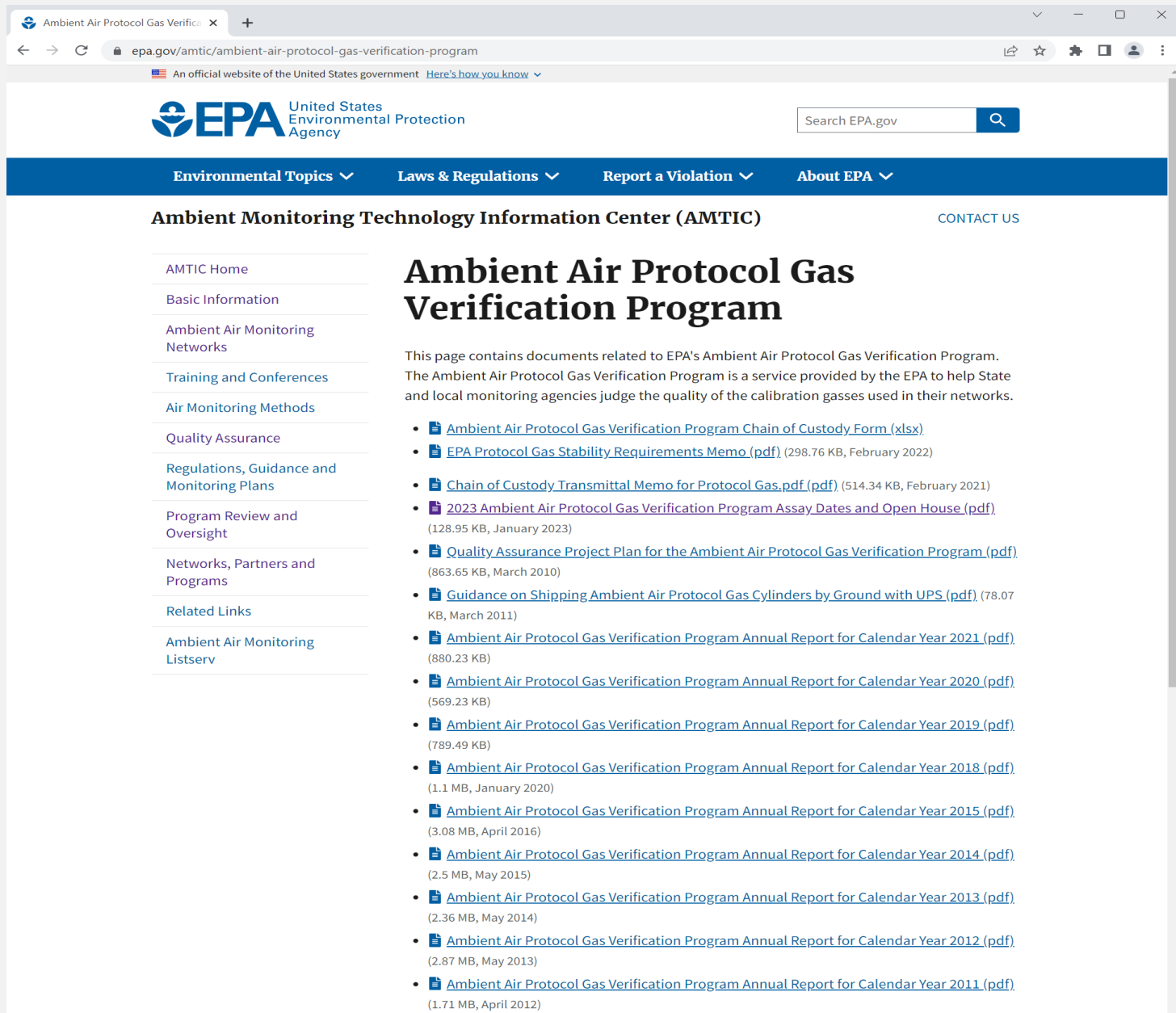
Overview

On and after May 27, 2011, the owner or operator of a unit subject to Part 75 emissions monitoring that uses EPA Protocol gases must procure the gases from a production site that is listed as a PGVP participant on the date that it procures the gases, or from a merchant who sells unaltered EPA Protocol gases produced by an EPA Protocol gases production site that is listed as a PGVP participant on the date that the merchant procured the gases. See [40 CFR 75.21\(g\)\(6\) and \(7\)](#). These gases and the associated quality assurance/quality control (QA/QC) checks help ensure the quality of the emission data that EPA uses to assess achievement of emission reductions required under the Clean Air Act.

Related Information

- [Request to Participate](#)
- [Fact Sheets](#)
- [Read the Rule](#)
- [Feedback or Questions](#)

The PGVP has four main objectives: (1) to ensure that EPA Protocol gases meet the accuracy requirements of 40 CFR Part 75; (2) to assist calibration gas consumers in their purchasing decisions; (3) to provide an incentive for gas vendors that perform well in the audits to continue to use good practices; and (4) to encourage gas vendors that perform poorly in the audits to make improvements.




The screenshot shows a web browser window displaying the EPA website. The address bar shows the URL: epa.gov/amtic/ambient-air-protocol-gas-verification-program. The page features the EPA logo and a search bar. A navigation menu includes: Environmental Topics, Laws & Regulations, Report a Violation, and About EPA. The main content area is titled "Ambient Monitoring Technology Information Center (AMTIC)" and includes a "CONTACT US" link. A sidebar on the left lists various categories: AMTIC Home, Basic Information, Ambient Air Monitoring Networks, Training and Conferences, Air Monitoring Methods, Quality Assurance, Regulations, Guidance and Monitoring Plans, Program Review and Oversight, Networks, Partners and Programs, and Related Links. The main heading is "Ambient Air Protocol Gas Verification Program". Below the heading, a paragraph states: "This page contains documents related to EPA's Ambient Air Protocol Gas Verification Program. The Ambient Air Protocol Gas Verification Program is a service provided by the EPA to help State and local monitoring agencies judge the quality of the calibration gasses used in their networks." A list of 15 documents follows, each with a PDF icon, a title, and file size/date information.

Ambient Air Protocol Gas Verifica x +

← → ↻ epa.gov/amtic/ambient-air-protocol-gas-verification-program 🔍 ⚙️ 🏠 👤 ⋮

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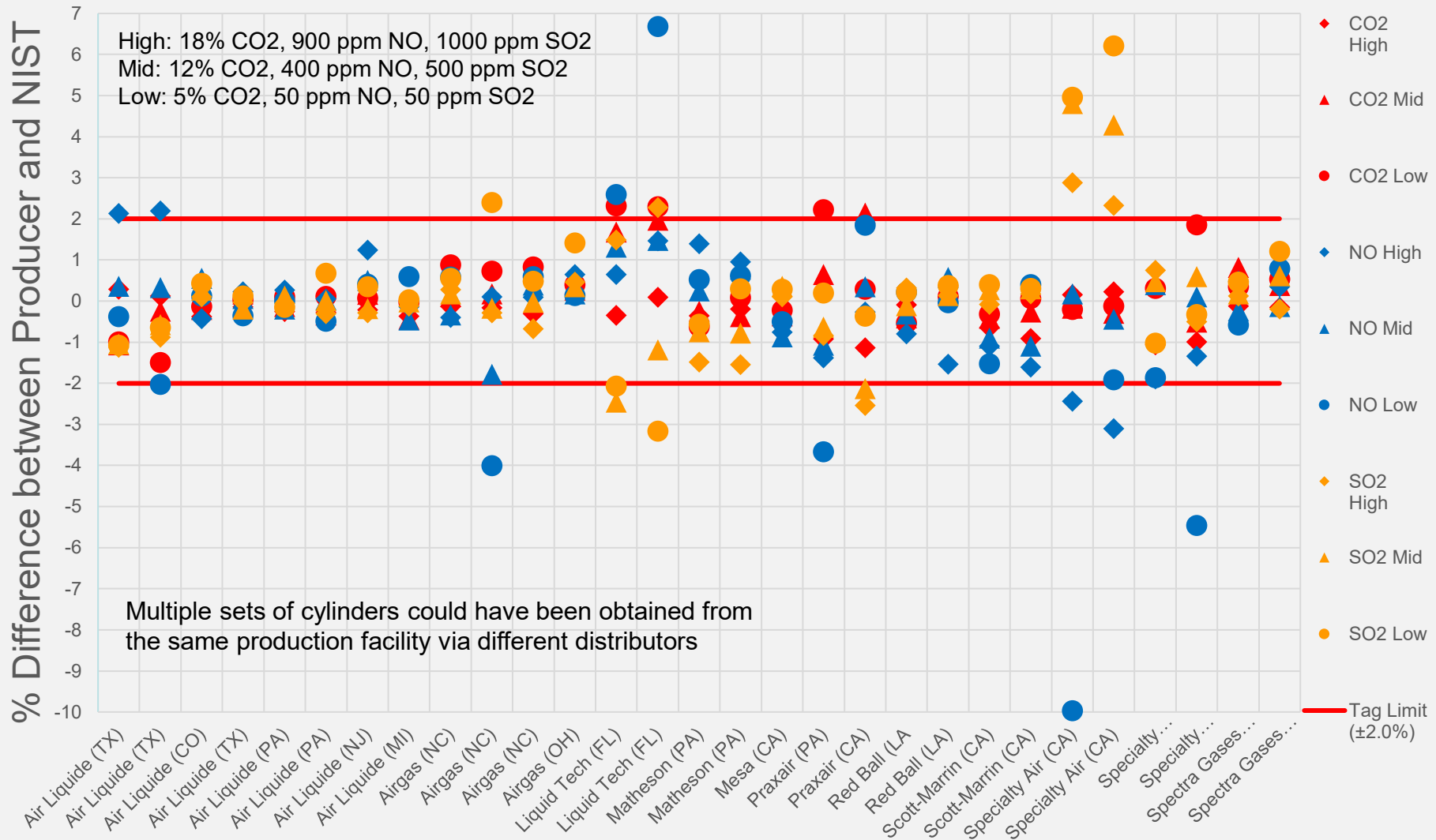
[Ambient Air Monitoring Listserv](#)

Ambient Air Protocol Gas Verification Program

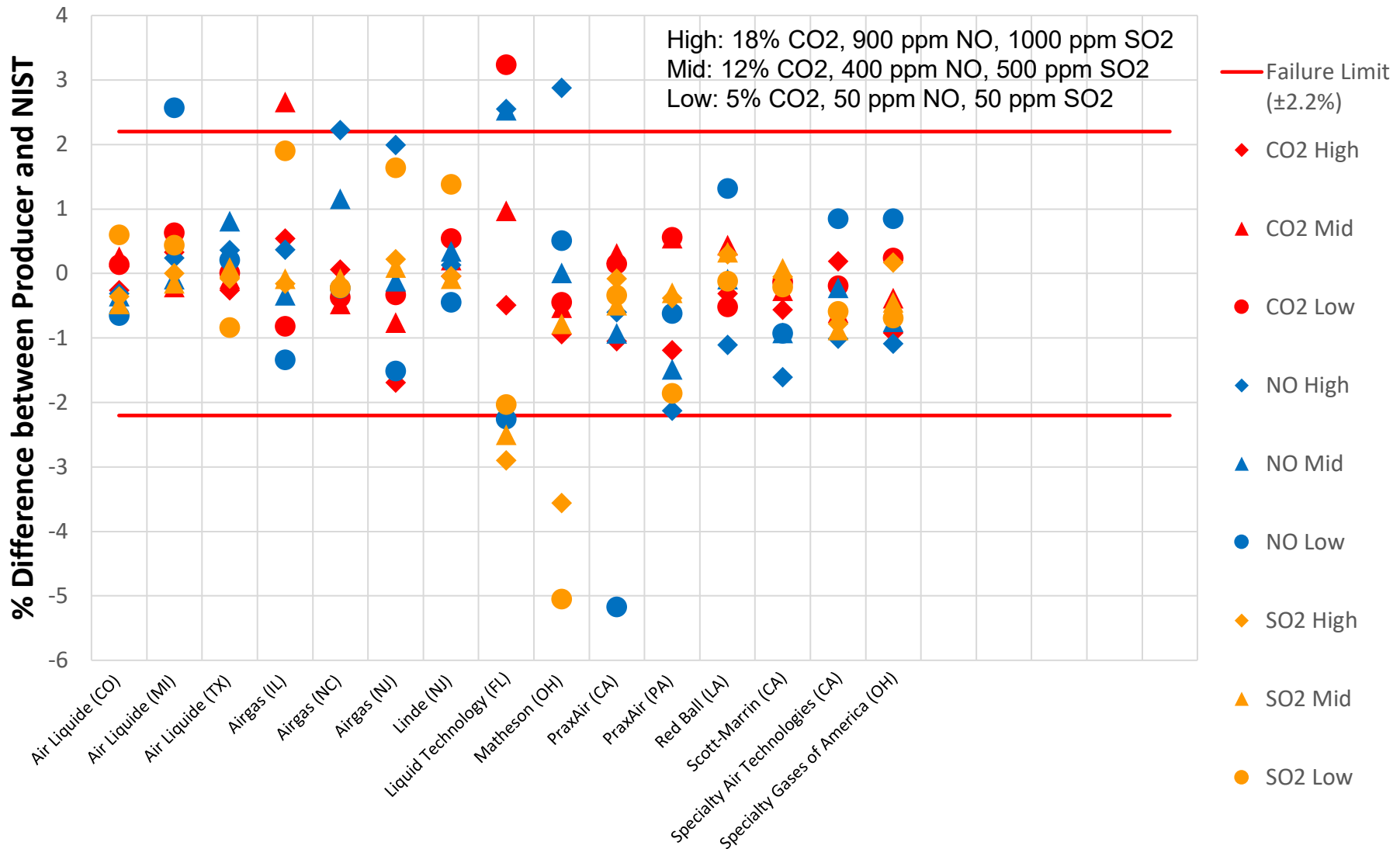
This page contains documents related to EPA's Ambient Air Protocol Gas Verification Program. The Ambient Air Protocol Gas Verification Program is a service provided by the EPA to help State and local monitoring agencies judge the quality of the calibration gasses used in their networks.

- [Ambient Air Protocol Gas Verification Program Chain of Custody Form \(xlsx\)](#)
- [EPA Protocol Gas Stability Requirements Memo \(pdf\)](#) (298.76 KB, February 2022)
- [Chain of Custody Transmittal Memo for Protocol Gas.pdf \(pdf\)](#) (514.34 KB, February 2021)
- [2023 Ambient Air Protocol Gas Verification Program Assay Dates and Open House \(pdf\)](#) (128.95 KB, January 2023)
- [Quality Assurance Project Plan for the Ambient Air Protocol Gas Verification Program \(pdf\)](#) (863.65 KB, March 2010)
- [Guidance on Shipping Ambient Air Protocol Gas Cylinders by Ground with UPS \(pdf\)](#) (78.07 KB, March 2011)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2021 \(pdf\)](#) (880.23 KB)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2020 \(pdf\)](#) (569.23 KB)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2019 \(pdf\)](#) (789.49 KB)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2018 \(pdf\)](#) (1.1 MB, January 2020)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2015 \(pdf\)](#) (3.08 MB, April 2016)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2014 \(pdf\)](#) (2.5 MB, May 2015)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2013 \(pdf\)](#) (2.36 MB, May 2014)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2012 \(pdf\)](#) (2.87 MB, May 2013)
- [Ambient Air Protocol Gas Verification Program Annual Report for Calendar Year 2011 \(pdf\)](#) (1.71 MB, April 2012)

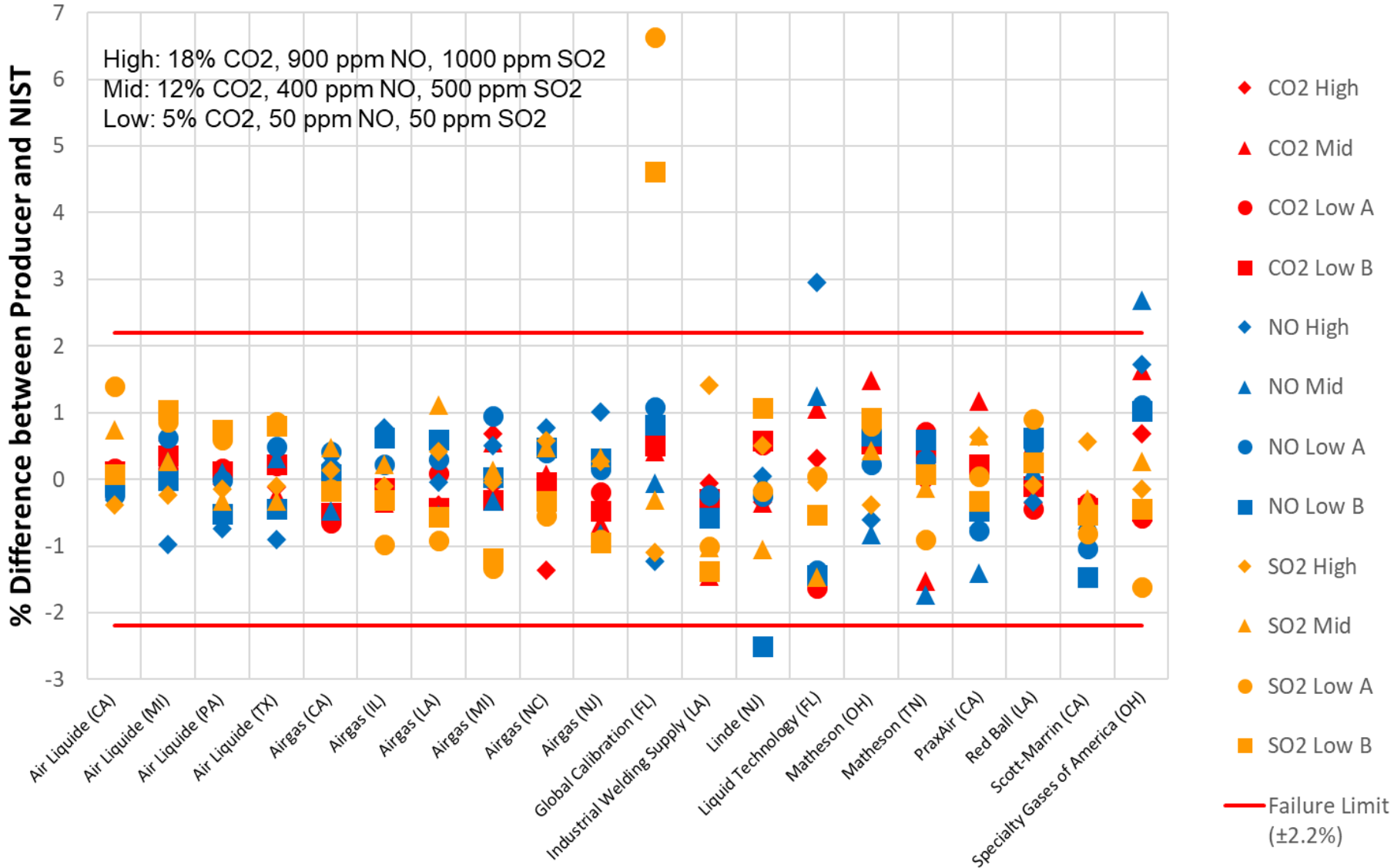
2008 EPA Inspector General Audit



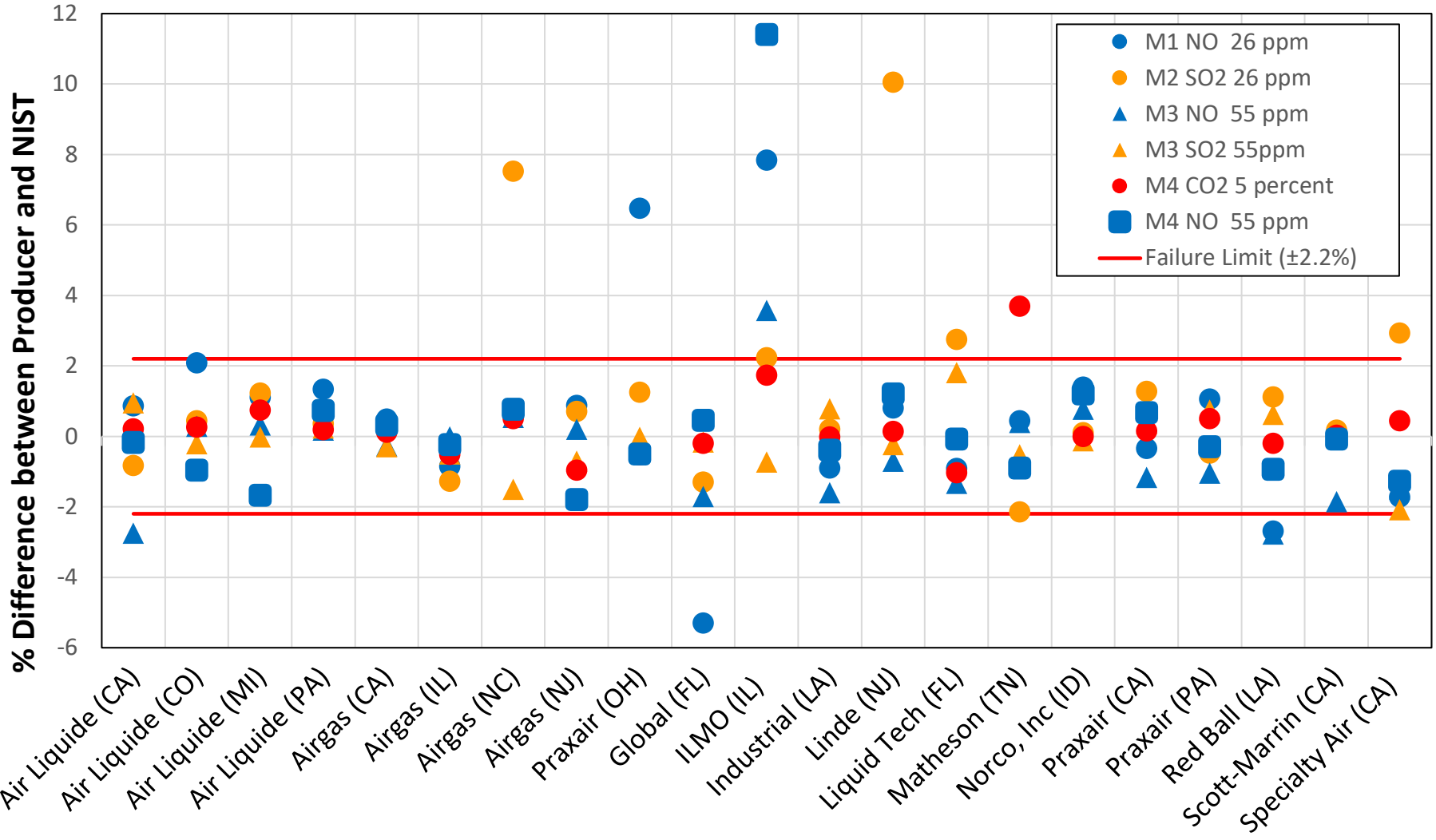
2010 Emission PGVP Results



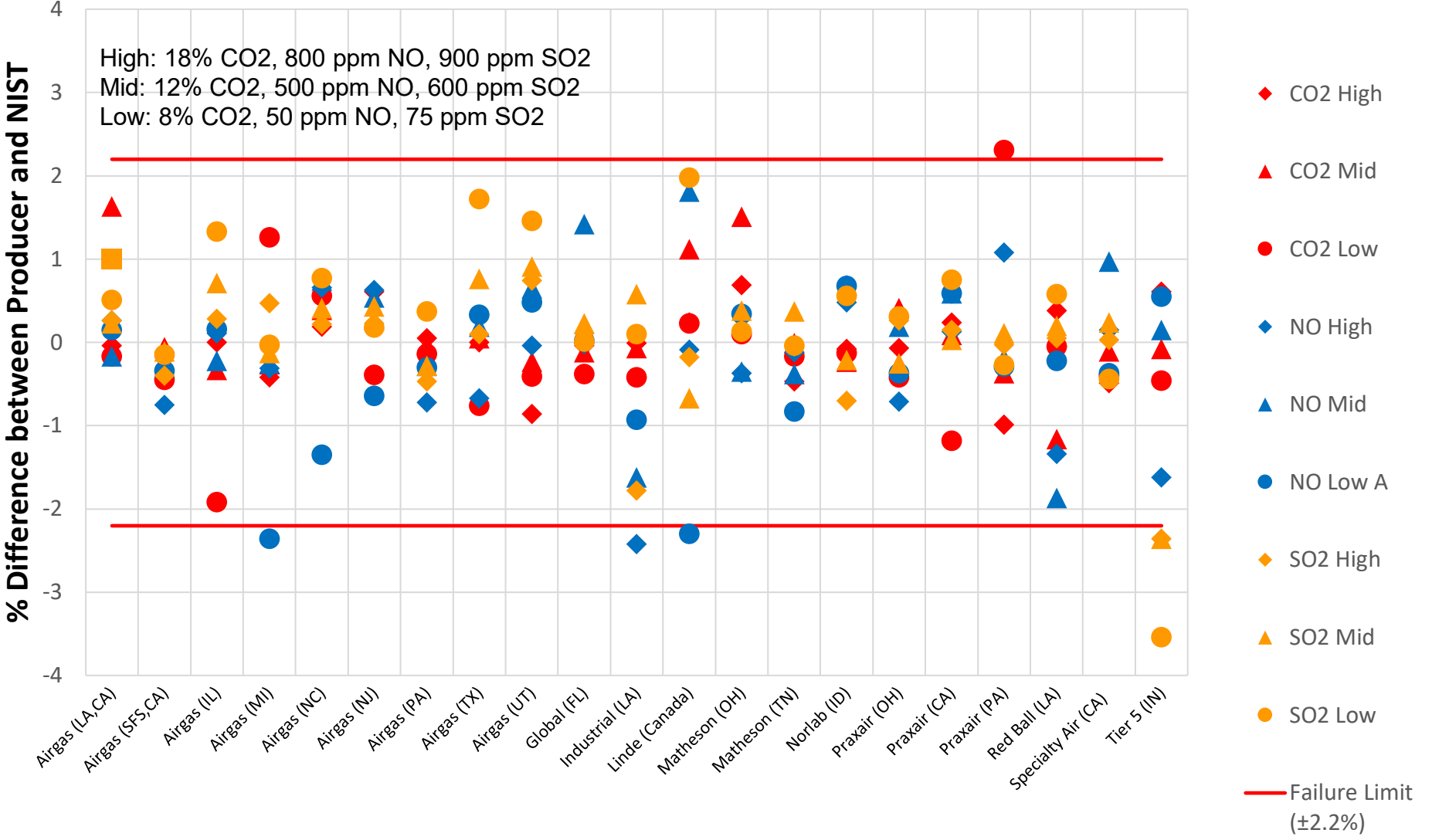
2013 Emission PGVP Results



2015 Emission PGVP Results



2018 Emission PGVP Results



Summary of Emission PGVP Results

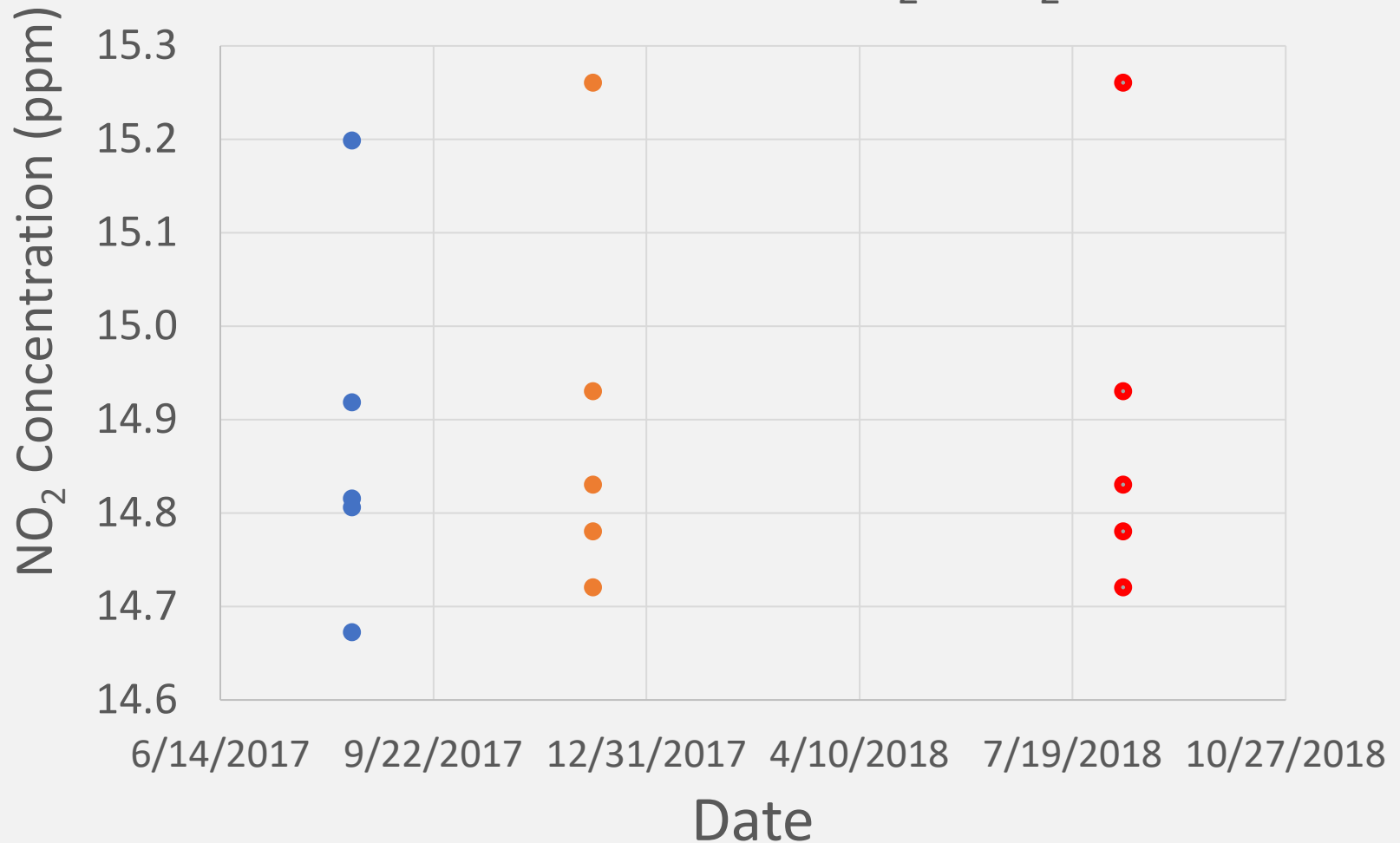
Year	Percentage within +/- 2.2 percent accuracy	Percentage within +/- 5.2 percent accuracy
2008	92	98
2010	90	99
2013	98	99+
2015	89	95
2018	94	100

Status of NO₂ EPA Protocol Gases

- In 2014, EPA allowed the use of direct-reading NO₂ ambient air analyzers that need NO₂ calibration gases
- NO₂ gas mixtures are generally not stable because NO₂ reacts with moisture on cylinder interior surfaces to form HNO₃ and then NO₂ concentration decays
- Two cylinder manufacturers have a special technology to passivate the interior surfaces for NO₂ stability
- Other cylinders have not demonstrated NO₂ stability
- EPA wrote in February 2022 that NO₂ gas mixtures cannot be used for regulatory monitoring under Section 2.6.1 of 40 CFR Part 58, Appendix A

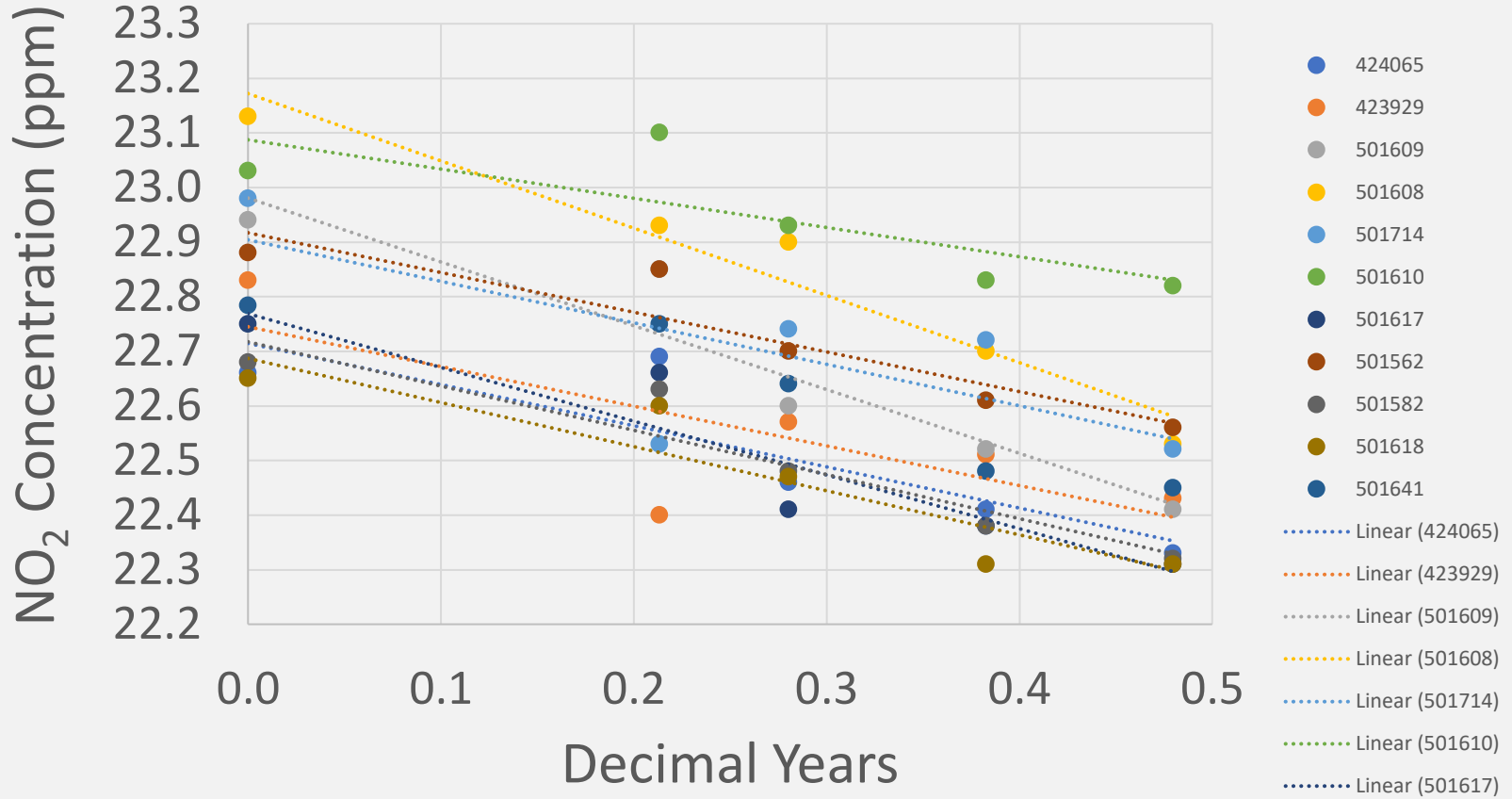
Example Stable NO₂ Gas Mixtures

5 Cylinders of 15 ppm NO₂ in N₂



Example Unstable NO₂ Gas Mixtures

11 Cylinders of 23 ppm NO₂ in Air
Decay Rates -0.5 to -1.2 ppm/year

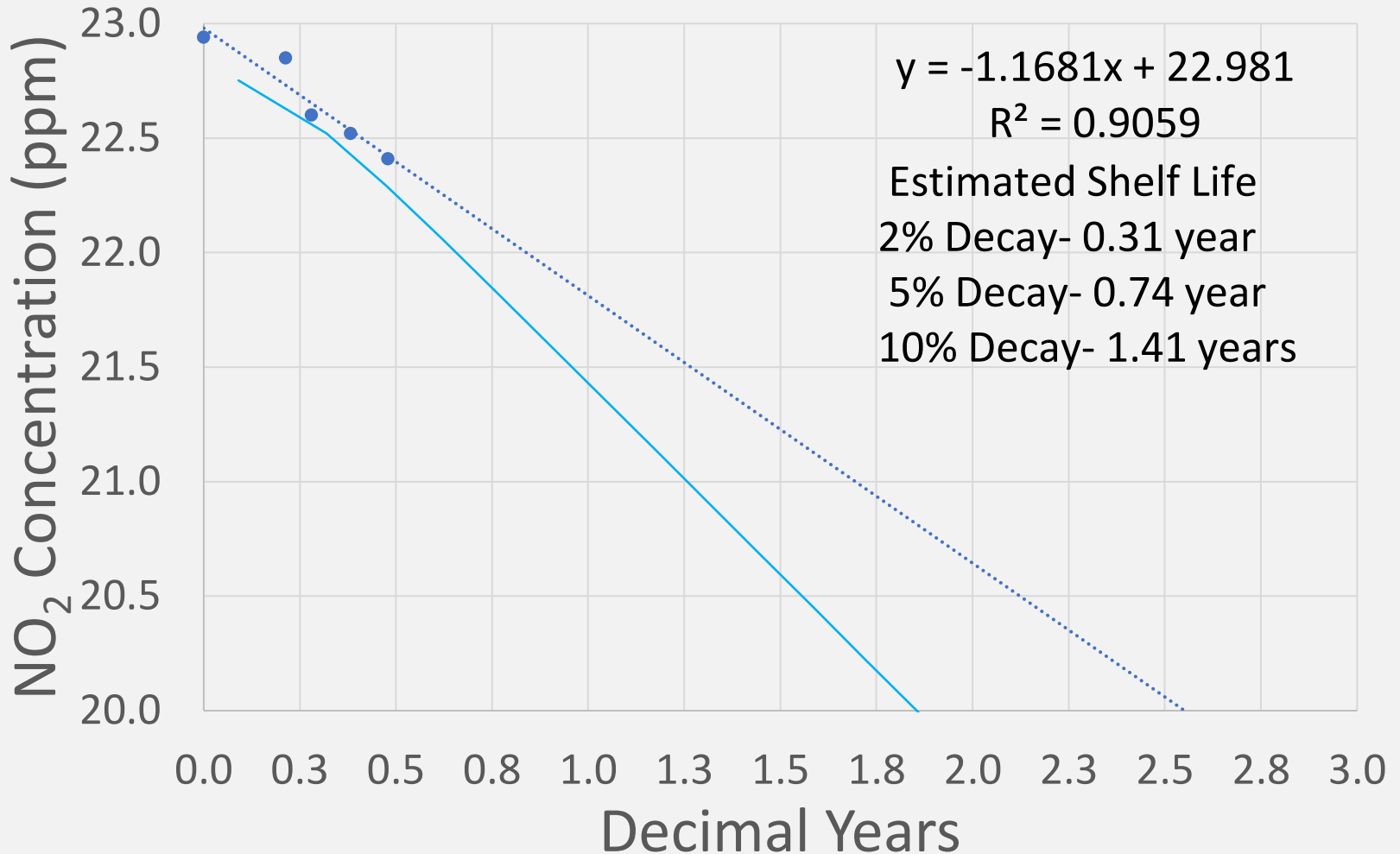


New Procedure for Reactive Gases

- EPA is preparing a new procedure that will allow producers to estimate the shelf lives for cylinders with decaying NO₂ concentrations
- 100-percent stability testing of reactive gas mixtures
- Multiple assays (e.g. 4) over test period (e.g., 6 mos.)
- Shelf lives estimated using statistical approach used by pharmaceutical industry (i.e., FDA, ISO Guide 35)
- Regression of stability data for one cylinder or a batch
- EPA specifies acceptable amount of decay (e.g., 2%)
- Lower 95% confidence interval for time to reach limit
- **Cylinder cost will be greater due to additional assays**
- **Delivery will be delayed due to longer testing period**

ISO Guide 35 used to estimate NO₂ shelf lives using linear regression

CYL 501609



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