

A Broad Overview of EPA Protocol Gases

Robert S. Wright
US Environmental Protection Agency
Research Triangle Park, NC 27711
wright.bob@epa.gov 919-541-4502

Outline of Presentation

- Basic concepts in gas metrology
- Regulatory requirements
- Historical background
- Reference materials for assays
- Types of EPA Protocol Gases
- Accuracy of EPA Protocol Gases
- Anticipated and needed reference standards

NIST Definition of Traceability

- Metrological traceability is defined as the 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**.
- NIST reference standard has an estimated uncertainty.
- Uncertainty accumulates 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 by regulated entities, such as governments, electric utilities, motor vehicle manufacturers, and aircraft engine manufacturers
- Legal and economic impacts of calibration inaccuracy justify 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); and
- 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 NBS Gaseous SRMs

- 1972 NBS-EPA Joint Conference on Development of Standard Reference Gases for Mobile Source Measurements
- Automotive and specialty gas producers attended
- NBS should concentrate on developing the technical specifications and certification procedures for gases
- Producers would supply batch blends in large cylinders for NBS to analyze, observe, and certify
- This division of labor utilizes the expertise of both groups and provides more assurance of gas availability in useable quantities
- SRMs are certified and sold by NIST (formerly NBS), but are commercially produced

Origin of EPA Protocol Gases

- 1977 EPA-Industry Quality Control Symposium
- NBS, automotive 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 NBS SRM or a producer's GMIS
- Monthly multipoint calibrations, daily 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

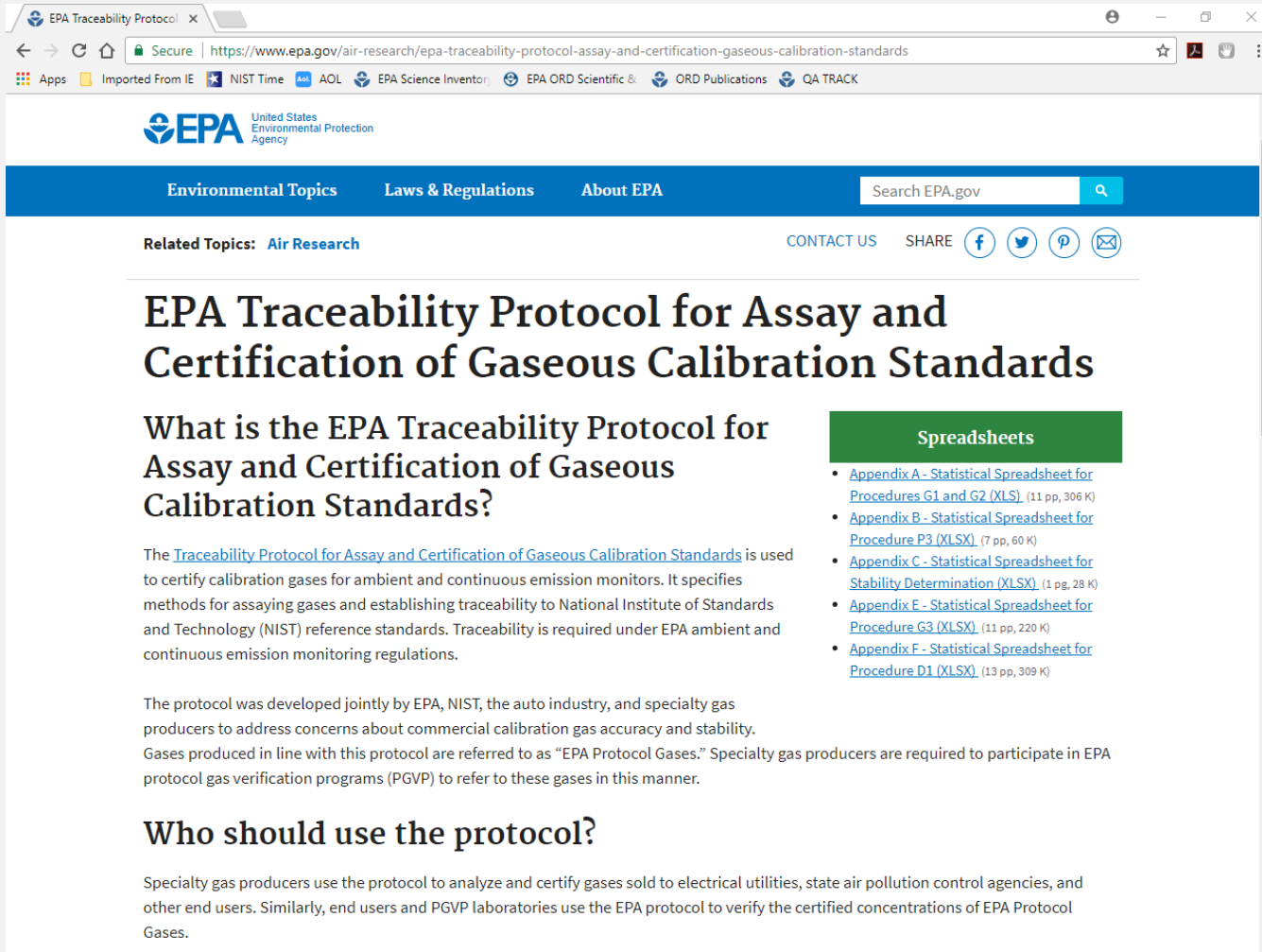
1978 EPA Traceability Protocol

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

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 with the URL <https://www.epa.gov/air-research/epa-traceability-protocol-assay-and-certification-gaseous-calibration-standards>. The page header includes the EPA logo and navigation links: Environmental Topics, Laws & Regulations, and About EPA. A search bar is also present. The main content area features the title 'EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards' and a subheading '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. A sidebar on the right lists several spreadsheets: Appendix A - Statistical Spreadsheet for Procedures G1 and G2 (XLS), Appendix B - Statistical Spreadsheet for Procedure P3 (XLSX), Appendix C - Statistical Spreadsheet for Stability Determination (XLSX), Appendix E - Statistical Spreadsheet for Procedure G3 (XLSX), and Appendix F - Statistical Spreadsheet for Procedure D1 (XLSX). The footer of the page includes the text 'Who should use the protocol?' and a paragraph explaining 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.

EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards

What is the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards?

The [Traceability Protocol for Assay and Certification of Gaseous Calibration Standards](#) 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.

Who should use the protocol?

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.

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)
- [Appendix F - Statistical Spreadsheet for Procedure D1 \(XLSX\)](#) (13 pp, 309 K)

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)
- Gas Manufacturer's Intermediate Standard (GMIS), which are analyzed using NIST reference standards
- The availability of reference standards remains the biggest obstacle to producing EPA Protocol Gases

NIST Priorities for Production of Reference Standards

- Production of new SRM batches
- QA for existing SRMs (e.g., stability studies)
- NTRM assay and certification
- RGM assay and certification
- Research into new reference materials

NIST NTRM Program Highlights

- Follow 2013 revision to NTRM document
- Producer must be accredited to ISO 17025
- Laboratory inspection by NIST
- Use new cylinders and valves for NTRMs
- Demonstrate effective cylinder passivation techniques
- Production of homogeneous cylinder batches
- Possess high-accuracy analytical instrumentation
- Possess NIST SRMs or VSL PRMs for calibration
- Competent staff in laboratory
- Sequester batch standard for NTRM recertifications
- Submit data and some cylinders to NIST for assay

NIST Pricing for NTRM Certification

Batch size

Base price*

• 10-20	\$6800
• 21-40	\$9200
• 41-60	\$11,600
• 61-80	\$14,000

* NIST audit of the batch standard and a 10% sample

Point-of-Contact: Michael E. Kelley

NIST Gas Metrology Group

301-975-5461 mekelley@nist.gov

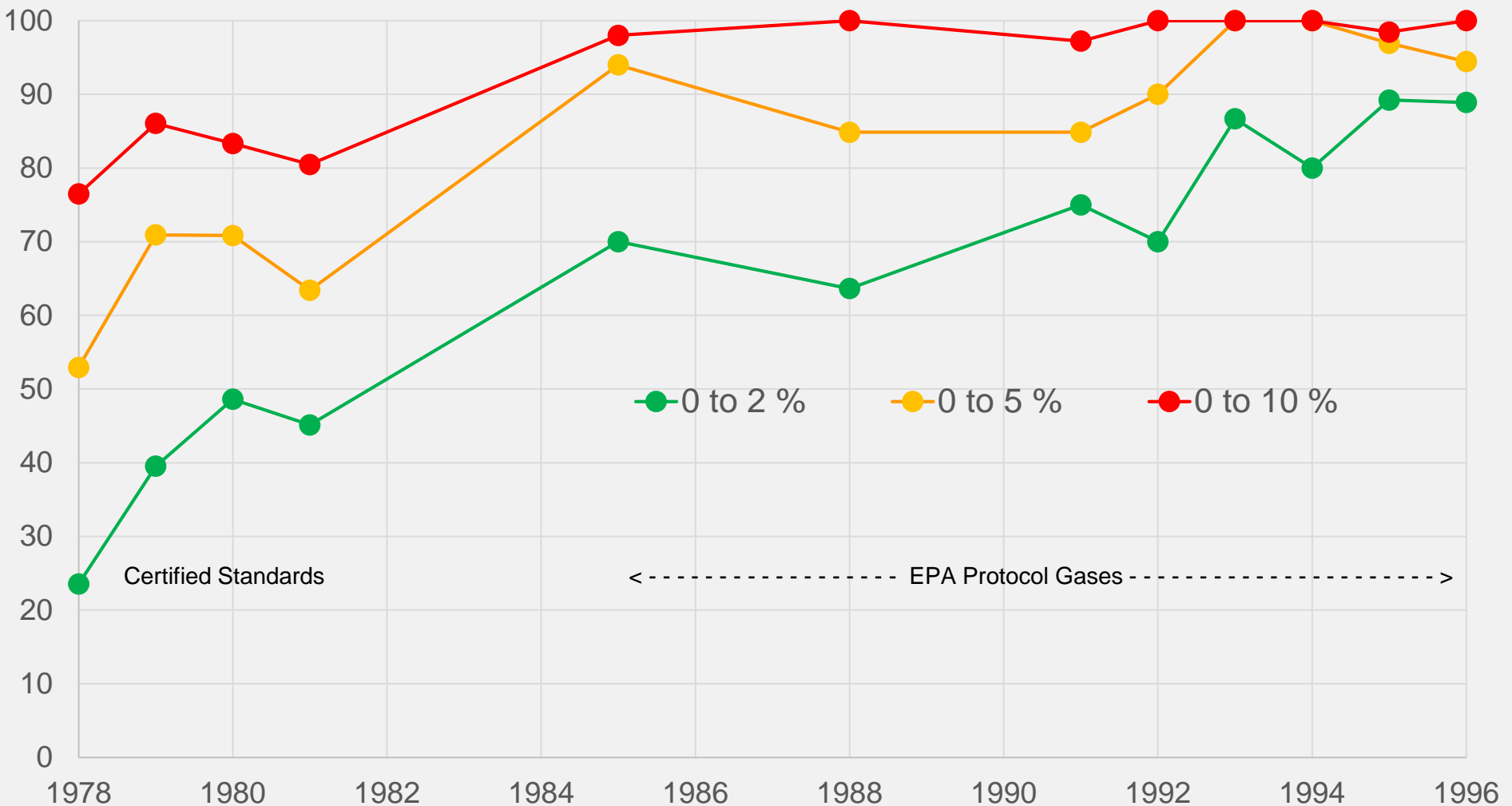
Maximum Certification Periods in Passivated Aluminum Cylinders

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 cylinders from 1978 through 1981
- Audits of EPA Protocol Gases from 1985 through 1996, then hiatus

Percentage of Audited Cylinder Gases within a Given Accuracy Range



Protocol Gas Verification Program

- EPA inspector general audited EPA Protocol Gases in 2008 and recommended restarting audit program
- Only PGVP participants and their vendors can sell EPA Protocol Gases
- Emissions PGVP purchased gases by third-party buyer with assay by NIST
- Ambient air PGVP obtained gases from agencies or directly from 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

Clean Air Markets

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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.

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.

2018 Participants and Vendor IDs

The list of current participants in EPA's Protocol Gas Verification Program (PGVP) for stationary source monitoring is updated: (1) at the beginning of each calendar year; (2) when an EPA Protocol gas production site joins the program; (3) when the information for a listed production site changes; or (4)

Related Information

- [Request to Participate](#)
- [Fact Sheets](#)
- [Read the Rule](#)
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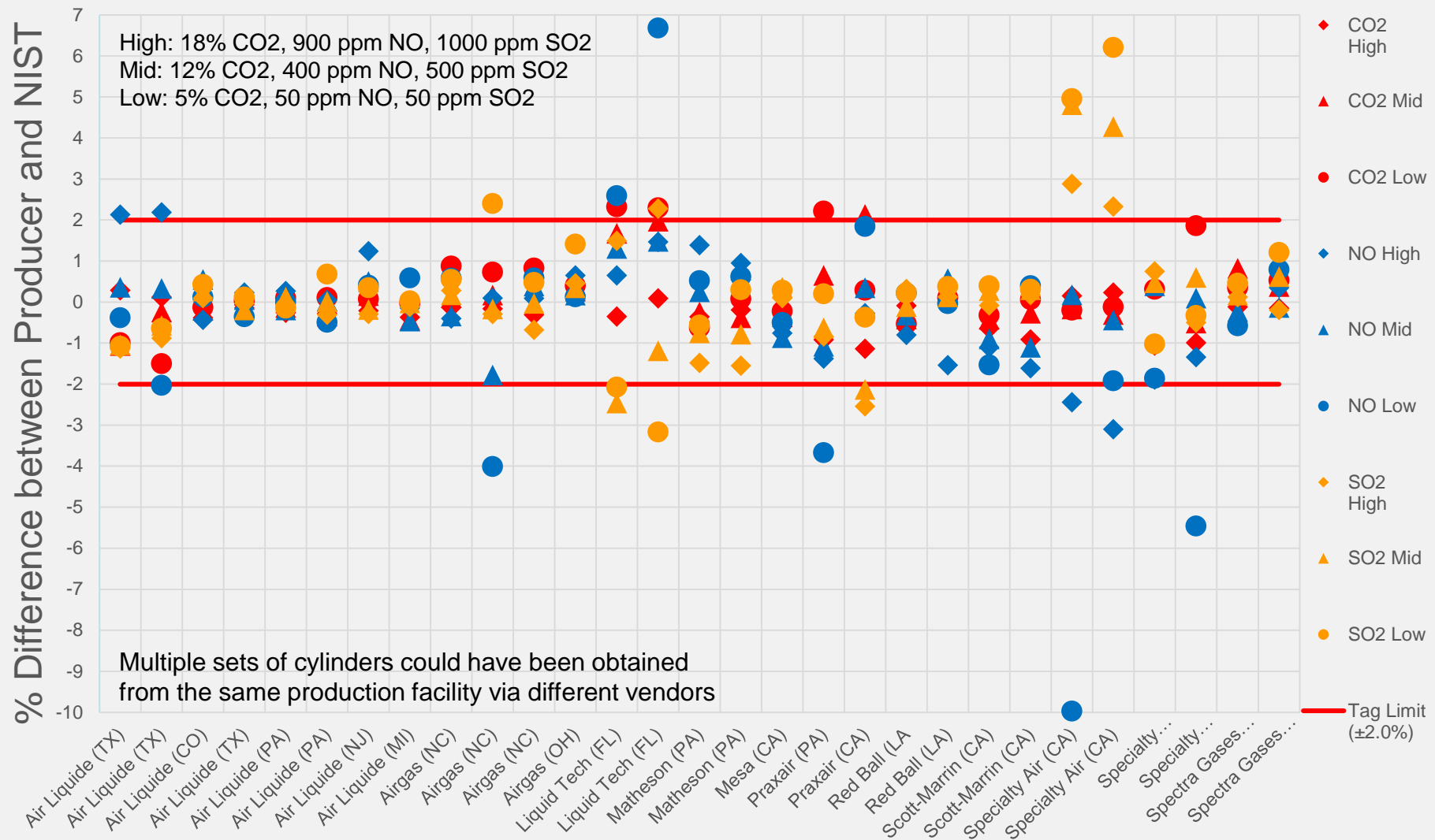
National Performance Evaluation Program – Ambient Air Protocol Gas Verification Program

- [2015 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (43pp, 2.5 MB)
- [2014 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (43pp, 2.5 MB)
- [2015 Ambient Air Protocol Gas Verification Program Verification Dates, Open House and Shipping Schedule \(PDF\)](#) (1pg, 200k)
- [2013 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (36pp, 2.4 MB)
- [2014 Ambient Air Protocol Gas Verification Program Verification Dates, Open House and Shipping Schedule \(PDF\)](#) (1pg, 252k)
- [2012 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (43pp, 2.9 MB) – May 2013
- [Producers Participating in the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (1pg, 14k) – April 2013
- [2013 Ambient Air Protocol Gas Verification Program Verification Dates, Open House and Shipping Schedule \(PDF\)](#) (1pg, 69k) – February 2013
- [2011 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (40pp, 1.7 MB) – April 2012
- [2012 Instructions for Shipping Gas Standards the Regional Verification Laboratories. \(PDF\)](#) (2pp, 18k) – June 2012
- [2010 Annual Report for the Ambient Air Protocol Gas Verification Program \(PDF\)](#) (32pp, 1.2 MB) – April 2011
- [EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards](#)
- [Guidance on shipping gas standards with UPS \(PDF\)](#) (2pp, 78k) – March 2011
- [April 15, 2010 Region 7 AA-PGVP Laboratory Technical Systems Audit \(PDF\)](#) (3pp, 22k) – May 2010
- [April 13, 2010 Region 2 AA-PGVP Laboratory Technical Systems Audit \(PDF\)](#) (3pp, 22k) – May 2010

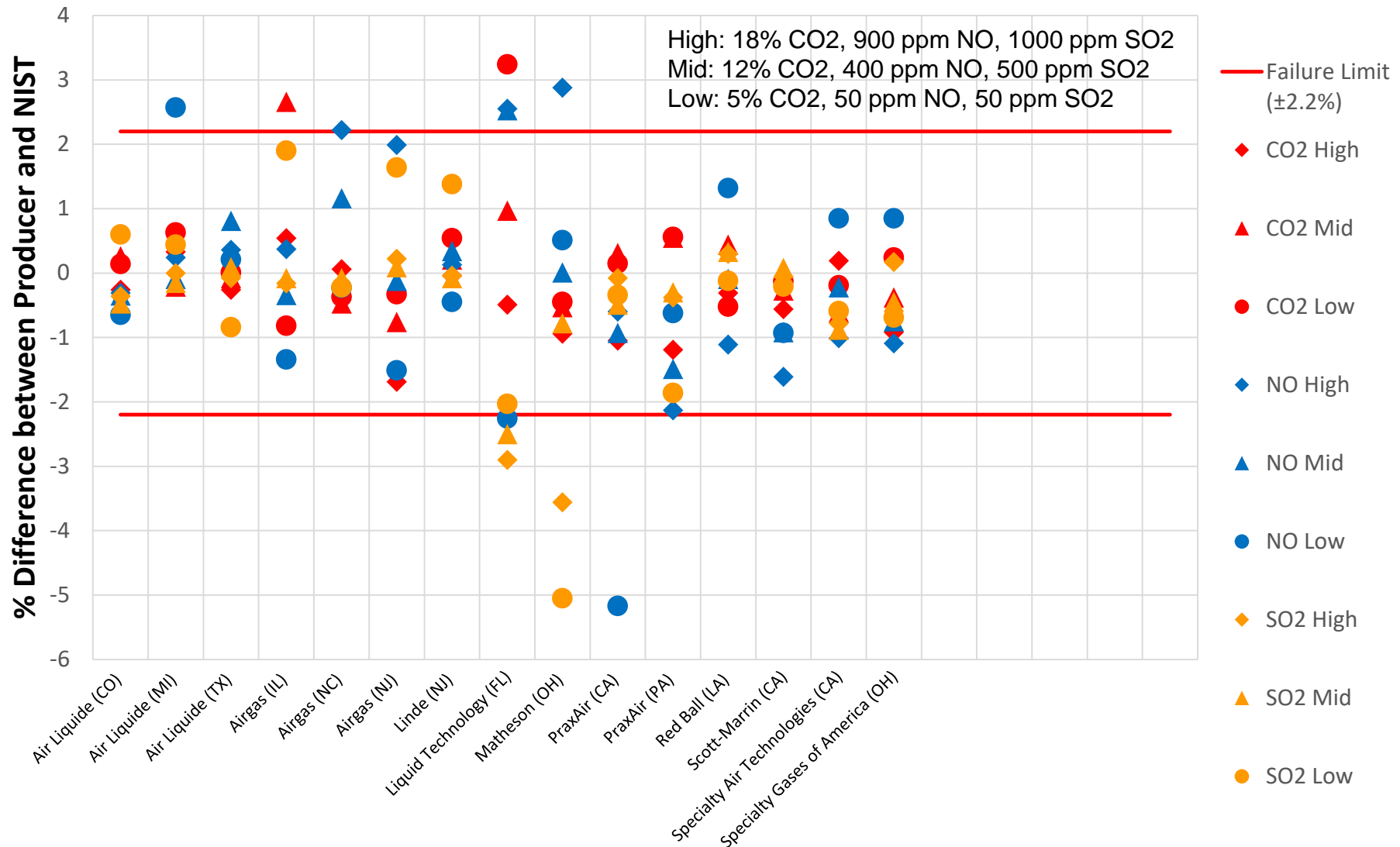
<https://www3.epa.gov/ttn/amtic/files/ambient/qaqc/2015verification.pdf>

[Air – Protocol Gas Verification Program Chain of Custody Form \(PDF\)](#) (1pg, 22k) – May 2010

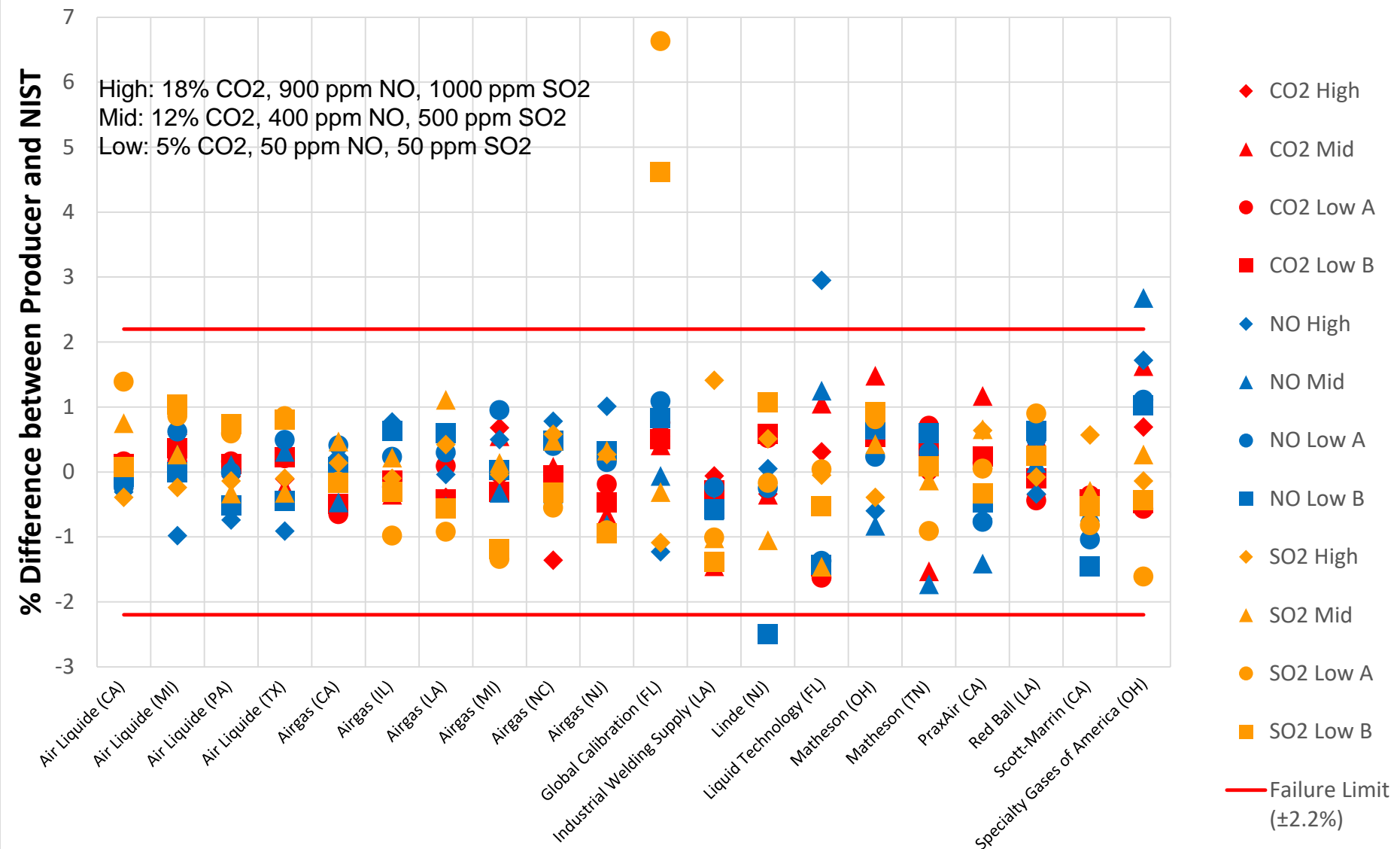
2008 EPA Inspector General Audit



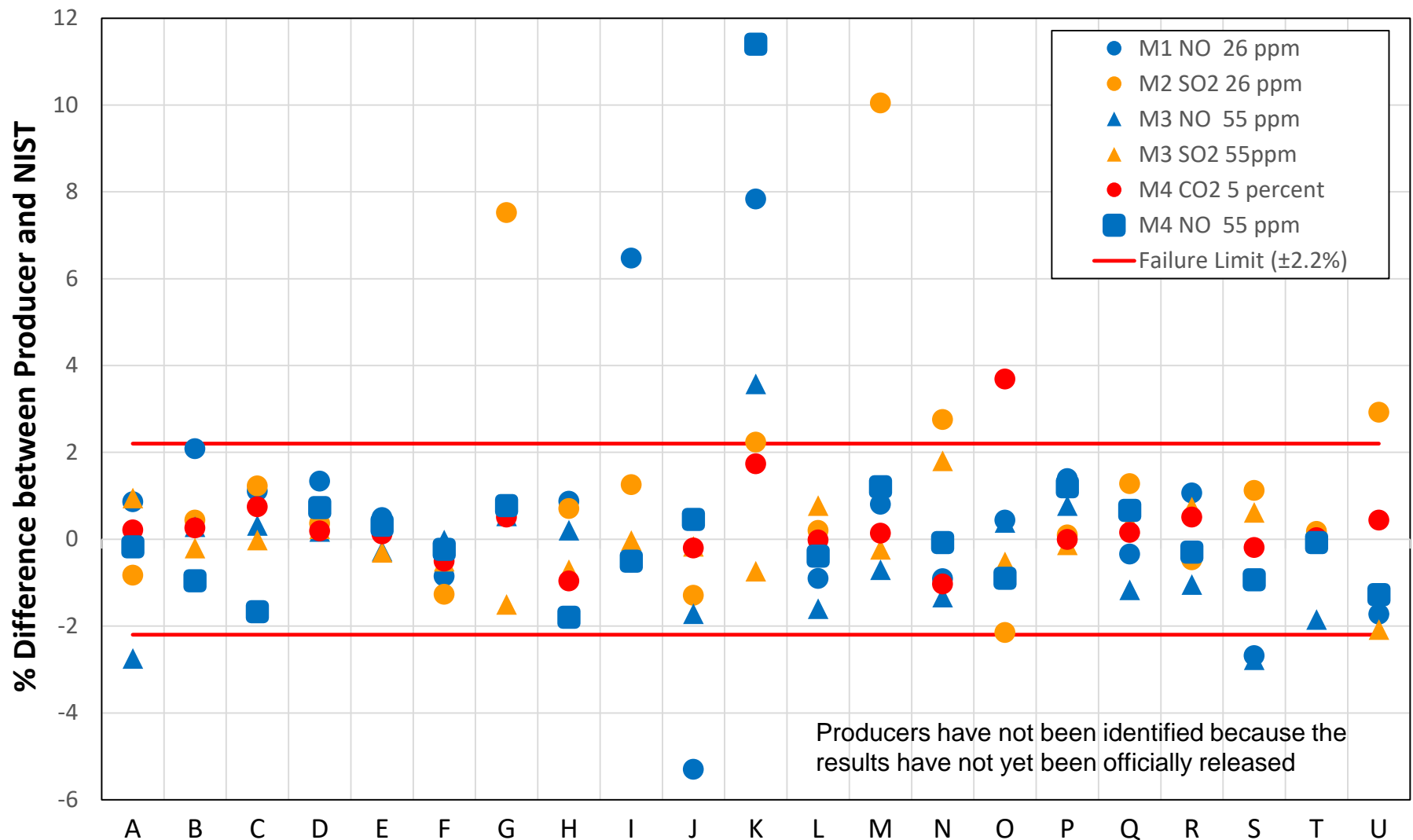
2010 Emission PGVP Results



2013 Emission PGVP Results



2015 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

PGVP Administrative Contacts

Emission PGVP- Travis Johnson

EPA Headquarters, Washington, DC

johnson.travis@epa.gov

202-343-9018

<https://www.epa.gov/airmarkets/protocol-gas-verification-program-pgvp>

Ambient Air PGVP- Solomon Ricks

EPA- Research Triangle Park, NC

ricks.solomon@epa.gov

919-541-5242

<https://www3.epa.gov/ttn/amtic/aapgvp.html>

SRMs being developed by NIST or needed by EPA

- Nitrogen dioxide (use VSL PRMs until SRM is ready)
- Hydrogen chloride (use ALT 114 until SRM is ready)
- Mercury (use ALT 118 until RGM is ready)
- Ammonia (need to expand range)
- Greenhouse gases in ambient air
- Sulfur hexafluoride
- Formaldehyde
- EPA wish list: HBr, HF, HCN, acrolein, ethylene oxide

EPA Alternative Methods 114 and 118

- These alternative methods will allow you prepare and certify HCl and Hg calibration gases as EPA Protocol Gases until such time as NIST SRMs become available
- EPA Office of Air Quality Planning and Standards can be petitioned regarding other gas mixtures
- EPA acceptance of an alternative test method shall be based on substantive technical support information
- See <https://www3.epa.gov/ttn/emc/approalt/alt114.pdf> and <https://www3.epa.gov/ttn/emc/approalt/alt118.pdf>
- Contact Ray Merrill (919-541-5225, merrill.raymond@epa.gov)

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