A Broad Overview of EPA Protocol Gases

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Outline of Presentation

- Traceability
- Regulatory monitoring requirements
- Historical background
- Reference materials for assays
- Types of EPA Protocol Gases
- Audits of EPA Protocol Gases
- Anticipated and needed reference standards
NIST Policy on Metrological 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

• Claims of traceability are the responsibility of the provider of the measurement result

• Assessing the validity of such a claim is the responsibility of the user of that result

• Traceability of gas mixtures is via reference gas mixtures rather than via reference mass standards
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 (NOx) 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
- SRMs to be prepared by producers and certified by NBS
- This division of labor utilizes the expertise of both groups and provides assurance of gas availability in useable quantities
- Four gas mixtures: $C_3H_8/\text{air}$; $CO_2/N_2$; $CO/N_2$; $NO/N_2$
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

- 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
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, 569 K)
- Appendix B - Statistical Spreadsheet for Procedure P3 (XLS) (7 pp, 46 K)
- Appendix C - Statistical Spreadsheet for Stability Determination (XLS) (12 pp, 14 K)
- Appendix D - Statistical Spreadsheet for Procedure G4 (XLS) (11 pp, 220 K)
- Appendix E - Statistical Spreadsheet for Procedure G1 (XLS) (13 pp, 300 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

<table>
<thead>
<tr>
<th>Batch size</th>
<th>Base price*</th>
</tr>
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<tbody>
<tr>
<td>10-20</td>
<td>$6800</td>
</tr>
<tr>
<td>21-40</td>
<td>$9200</td>
</tr>
<tr>
<td>41-60</td>
<td>$11,600</td>
</tr>
<tr>
<td>61-80</td>
<td>$14,000</td>
</tr>
</tbody>
</table>

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

Point-of-Contact: Michael E. Kelley
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301-975-5461 mekelley@nist.gov
### Maximum Certification Periods in Passivated Aluminum Cylinders

<table>
<thead>
<tr>
<th>Components</th>
<th>Balance gas</th>
<th>Concentration range</th>
<th>Period (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient VOCs</td>
<td>Nitrogen</td>
<td>1 ppb to 1 ppm</td>
<td>4</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Nitrogen</td>
<td>5 to 50 ppm</td>
<td>2</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Air</td>
<td>100 to 500 ppm</td>
<td>8</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Nitrogen</td>
<td>10 ppm to 20%</td>
<td>8</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Air</td>
<td>1 ppm to 10%</td>
<td>8</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Nitrogen</td>
<td>1 ppm to 15%</td>
<td>8</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Nitrogen</td>
<td>0.5 to 10 ppm</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>Nitrogen</td>
<td>10 to 5000 ppm</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>Nitrogen</td>
<td>5 to 1000 ppm</td>
<td>3</td>
</tr>
<tr>
<td>Methane</td>
<td>Air</td>
<td>1 to 1000 ppm</td>
<td>8</td>
</tr>
<tr>
<td>Methanol or ethanol</td>
<td>Nitrogen or Air</td>
<td>75 to 500 ppm</td>
<td>4</td>
</tr>
<tr>
<td>Natural gas components</td>
<td>Natural gas</td>
<td>Contact NIST</td>
<td>8</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>O₂-free nitrogen</td>
<td>0.5 to 20 ppm</td>
<td>3</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>O₂-free nitrogen</td>
<td>20 ppm to 1%</td>
<td>8</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>Nitrogen or Air</td>
<td>1 ppm to 1%</td>
<td>TBD</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>Air</td>
<td>TBD by NIST</td>
<td>6</td>
</tr>
<tr>
<td>Oxides of nitrogen</td>
<td>Air</td>
<td>10 ppm to 1%</td>
<td>6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Nitrogen</td>
<td>10 ppm to 25%</td>
<td>8</td>
</tr>
<tr>
<td>Propane</td>
<td>Air</td>
<td>0.1 to 500 ppm</td>
<td>8</td>
</tr>
<tr>
<td>Propane</td>
<td>Nitrogen</td>
<td>100 ppm to 2%</td>
<td>8</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>Nitrogen</td>
<td>1 to 50 ppm</td>
<td>4</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>Nitrogen</td>
<td>50 ppm to 1%</td>
<td>8</td>
</tr>
<tr>
<td>Zero air material</td>
<td>Air</td>
<td>Not applicable</td>
<td>Unlimited</td>
</tr>
<tr>
<td>Multicomponent mixtures</td>
<td>—</td>
<td>—</td>
<td>See text</td>
</tr>
<tr>
<td>Mixtures with lower concentrations</td>
<td>—</td>
<td>—</td>
<td>See text</td>
</tr>
</tbody>
</table>
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

0 to 2 %
0 to 5 %
0 to 10 %

Certified Standards
EPA Protocol Gases

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
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) when a site no longer meets the criteria to participate.
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) (30pp, 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-PAE Laboratory Technical Systems Audit (PDF) (3pp, 22k) – May 2010
- April 13, 2010 Region 2 AA-PAE Laboratory Technical Systems Audit (PDF) (3pp, 22k) – May 2010
Multiple sets of cylinders could have been obtained from the same production facility via different vendors.
2010 Emission PGVP Results

<table>
<thead>
<tr>
<th>CO2</th>
<th>NO</th>
<th>SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>High: 18% CO2, 900 ppm NO, 1000 ppm SO2</td>
<td>Mid: 12% CO2, 400 ppm NO, 500 ppm SO2</td>
<td>Low: 5% CO2, 50 ppm NO, 50 ppm SO2</td>
</tr>
</tbody>
</table>

% Difference between Producer and NIST

Failure Limit (±2.2%)

- CO2 High
- CO2 Mid
- CO2 Low
- NO High
- NO Mid
- NO Low
- SO2 High
- SO2 Mid
- SO2 Low
High: 18% CO2, 900 ppm NO, 1000 ppm SO2
Mid: 12% CO2, 400 ppm NO, 500 ppm SO2
Low: 5% CO2, 50 ppm NO, 50 ppm SO2
Producers have not been identified because the results have not yet been officially released.
## Summary of Emission PGVP Results

<table>
<thead>
<tr>
<th>Year</th>
<th>Percentage within +/- 2.2 percent accuracy</th>
<th>Percentage within +/- 5.2 percent accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>92</td>
<td>98</td>
</tr>
<tr>
<td>2010</td>
<td>90</td>
<td>99</td>
</tr>
<tr>
<td>2013</td>
<td>98</td>
<td>99+</td>
</tr>
<tr>
<td>2015</td>
<td>89</td>
<td>95</td>
</tr>
</tbody>
</table>
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
• Contact Ray Merrill (919-541-5225, merrill.raymond@epa.gov)
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