

# Protocol Gas Verification Program (PGVP)

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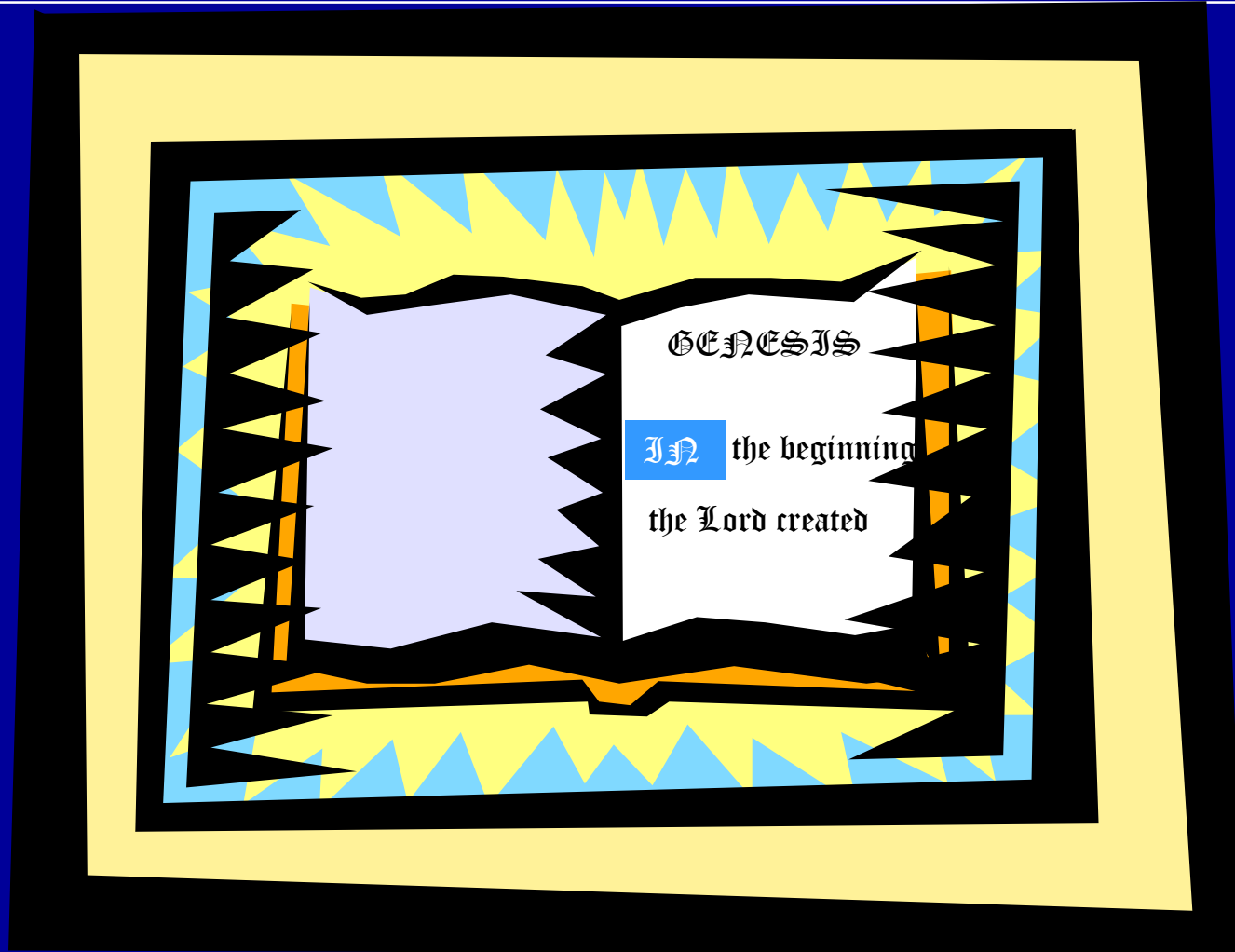
# PGVP

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- Protocol Gases from an historic perspective
- Historical Audit
- The PGVP



# Protocol Gases From an Historic Perspective



# Protocol Gases From an Historic Perspective

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- Calibration of CEMS to NIST traceable standards
  - Only “traceable” standards available were SRMs
  - SRMs only available in limited quantities and or concentrations also “small cylinder (800 l)”
  - EPA and NIST developed EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards



# Protocol Gases From an Historic Perspective

The Green Book

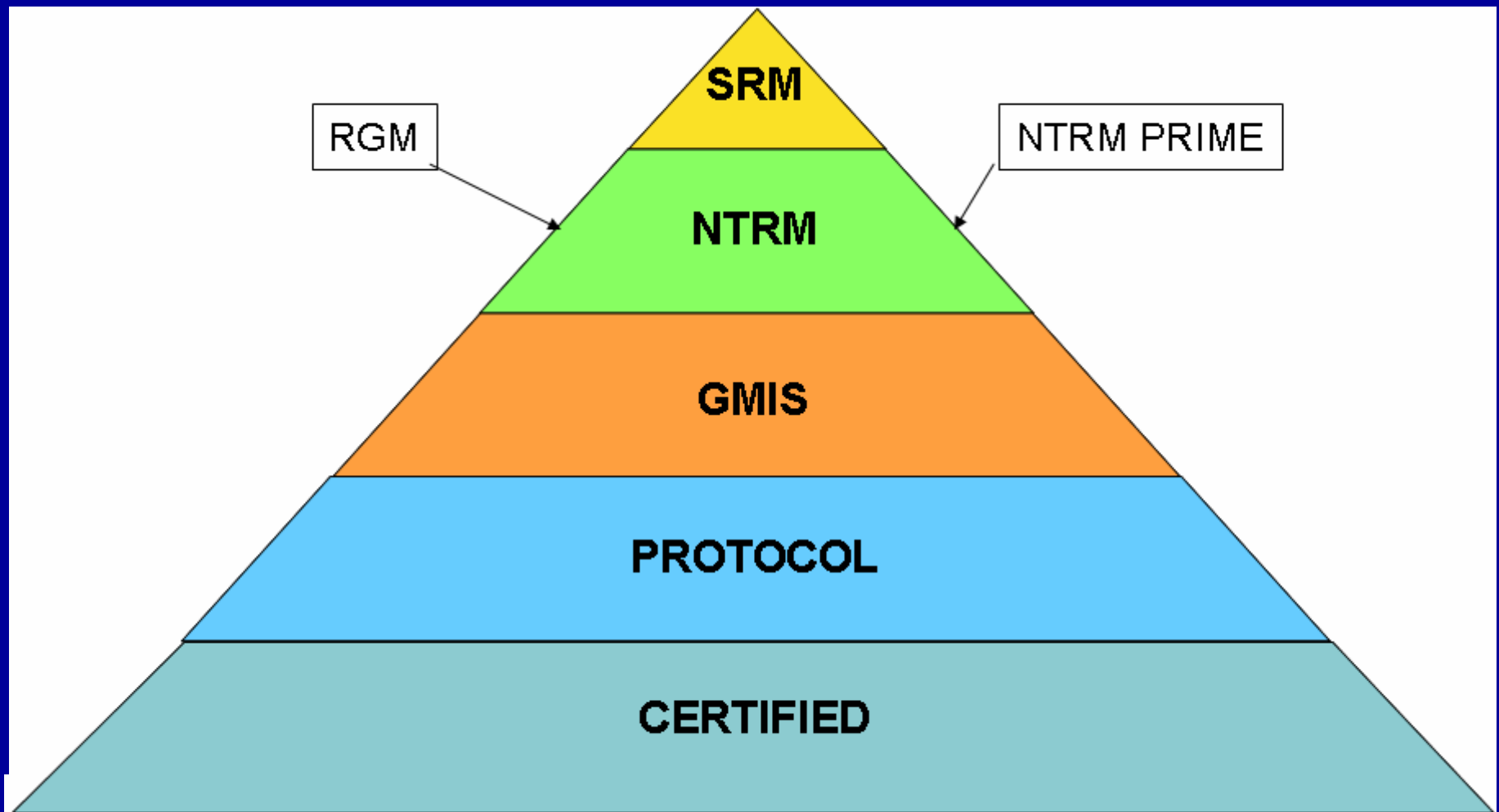
EPA-600/R-97/121

EPA TRACEABILITY PROTOCOL FOR ASSAY AND  
CERTIFICATION OF GASEOUS CALIBRATION STANDARDS

September 1997  
U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Human Exposure and Atmospheric Science Division  
Research Triangle Park, NC 27711



# Protocol Gases From an Historic Perspective



# Protocol Gases From an Historic Perspective

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- Primary Standard
- SRM
  - Standard Reference Material
- NTRM
  - NIST Traceable Reference Material
- GMIS
  - Gas Manufacturer's Internal Standard



# Primary Standard

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- Produced by NIST using gravimetric procedures
- Analyzed via two or more independent methods over time to confirm concentration
- Maintained at NIST (Gaithersburg, MD)



# Standard Reference Material

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- Produced under contract to NIST by a specialty gas company (currently only two companies manufacture for NIST)
- NIST analyzes each cylinder over time to confirm concentration. Analysis is directly traceable to PRM.
- Sold by NIST



# NIST Traceable Reference Material

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- Produced by a Specialty Gas Manufacturer in a batch; for cylinder to cylinder homogeneity (currently 4 companies produce NTRMs)
- Cylinders are analyzed over time
- Data is reported to NIST
- NIST requests at least 10% of the batch be sent to NIST and NIST performs its own analysis
- NIST “names” the batch
- NTRMs can have less uncertainty than SRMs



# NIST Traceable Reference Material



The image shows a white label for a NIST Traceable Reference Material (NTRM) Gas Mixture Standard. At the top center is the NIST logo, which consists of the letters "NIST" inside a diamond shape. Below the logo, the text reads "NIST Traceable Reference Material (NTRM<sup>CM</sup>)" and "Gas Mixture Standard". The label contains several key pieces of information:

Cylinder Number:	CC237212
Batch Producer:	Spectra Gases
NTRM Sample Number:	07100119
Mixture Contents:	Oxygen
Balance Gas:	Nitrogen
Certified Value:	(24.52 ± 0.12) % mol/mol
Date Certificate Issued:	March 13, 2007
Certificate Expires:	May 1, 2011

At the bottom of the label, the following text is printed: "National Institute of Standards and Technology", "Analytical Chemistry Division", "100 Bureau Drive, Stop 8393", and "Gaithersburg, MD 20899-8393". On the left side of the label, there is a vertical red stamp that reads "Laser" and "5168™".



# Gas Manufacturer's Internal Standard

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- Produced by a Specialty Gas Manufacturer following the “Green Book”
- Cylinders are analyzed over time vs. SRM or NTRM following the “Green Book”
- Cylinder is named by manufacturer



# Protocol Gases From an Historic Perspective

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- RGM – Research Gas Material
  - NIST named cylinder for which there is not the demand and/or the “politics” to have an SRM.
- NTRM Prime
  - Similar to NTRMs except NIST analyzes and names each cylinder. Driven by the auto industry to minimize uncertainty of tail pipe emissions data



# Protocol Gas

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- Manufactured and analyzed following the green book.
  - Single analysis for “non-reactives”
  - Dual analysis one week apart for “reactives”
- Analyzed against
  - SRM
  - NTRM / NTRM Prime / RGM
  - GMIS



# Minimum Requirements for U.S. EPA Protocol Gases

The following is the minimum information to be included when reviewing the certification documentation for U.S. EPA Protocol gases.

- 1. Cylinder identification number (serial number).
- 2. Certified concentration within three digits of the standard (ppm or % -mole basis).
- 3. Balance gas in the standard mixture.
- 4. Cylinder pressure at time of certification.
- 5. Assay/Certification date.
- 6. Certification expiration date.
- 7. Reference standard identification (standard type [SRM, PRM, NTRM, or GMIS], cylinder number and concentration).
- 8. Statement that the assay/certification conforms to EPA protocol guidelines.
- 9. Analytical method used.
- 10. Laboratory identification number (laboratory name, laboratory address).
- 11. Chronology of previous EPA protocol gas certification for this cylinder.
- 12. Analytical accuracy of the mixture.
- 13. Statement that certification was corrected for interference's (if applicable).
- 14. Ensure the concentration certified by the vendor matches the cylinder label value.



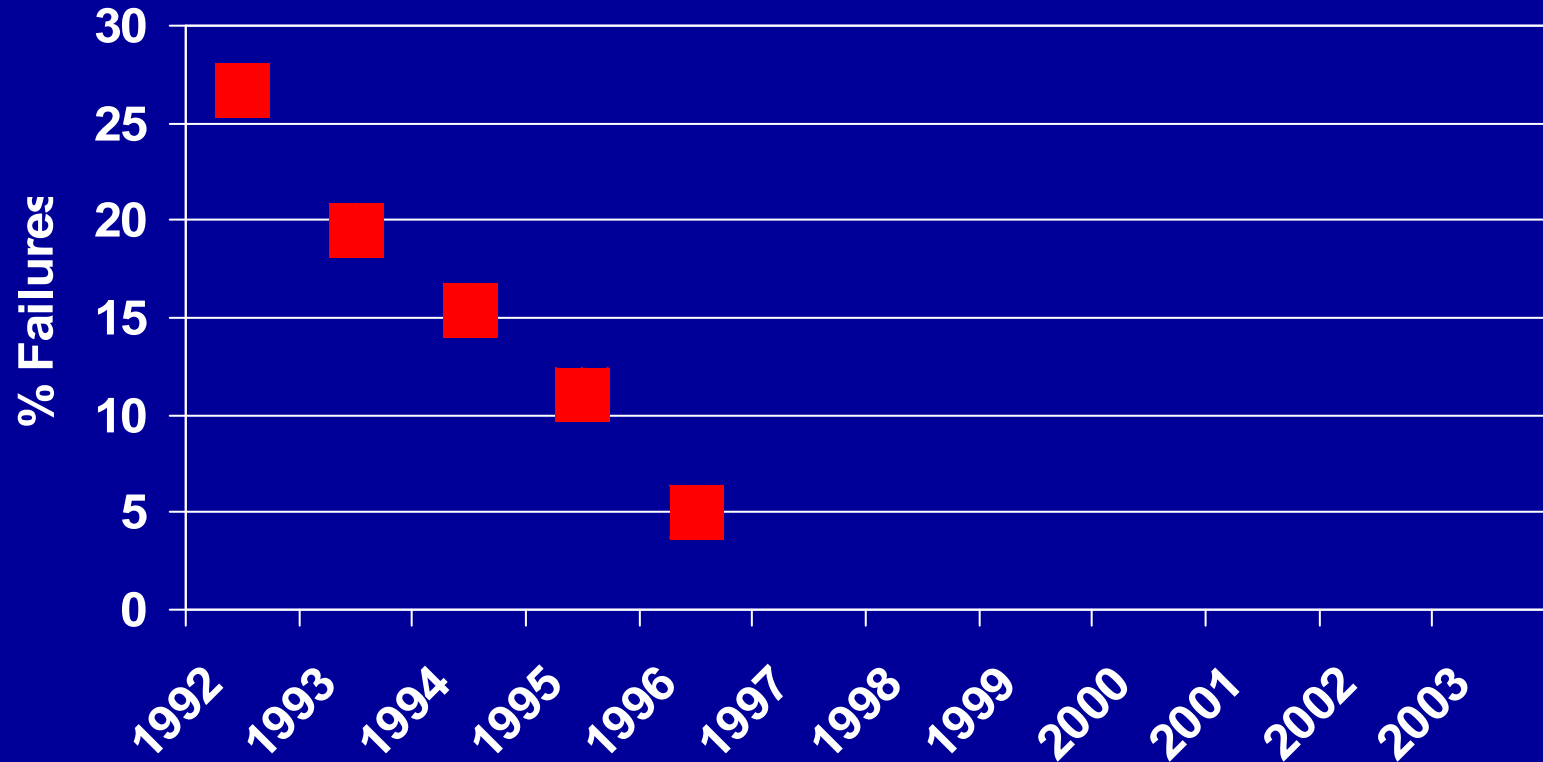
# Audit History of Protocols

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- 1970's -1996 EPA audited gases
- Posted results
  - In 1995, one vendor off by -16.3% (CEM would underreport)
- Strong utility and vendor support
- Auditing strongly correlated with improved gas quality
- Audit discontinued after 1996 due to budgetary constraints
- Audit reinitiated in 2003



# Audit Results



# 2003 Gas Audit

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- First audit in 7 years
- Blind audit
- 14 national gas vendors
- Similar procedures as in past
- SRMs and NTRMs used
- 42 Protocol tri-blend cylinders



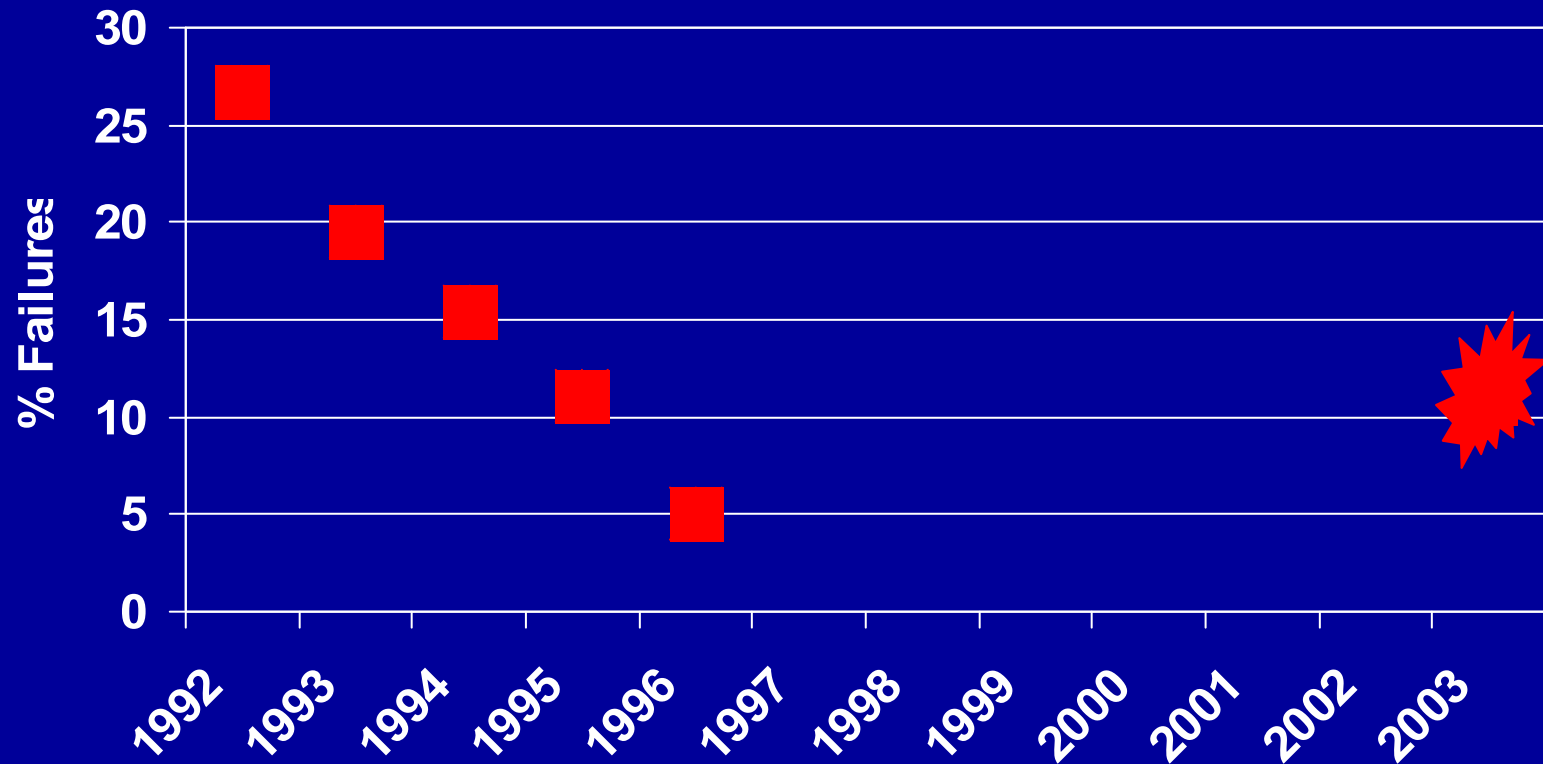
# Results

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- Overall failure rate: 14 of 126 analyses (11%)
- 57% of vendors failed
- SO<sub>2</sub>: Worst tag value ~2.5% high
- NO: Worst tag value ~8% low
- CO<sub>2</sub>: Worst tag value ~4.9% high
- All 42 cylinders met the Protocol Procedure documentation requirements



# Audit Results



EPA wants to improve and  
maintain the quality of US  
EPA Protocol gases thus

PGVP



# Part 58 (ambient) 1/17/06

provides national uniformity in the assurance and reporting of data quality for all networks, specific assessment and reporting procedures are prescribed in detail in sections 5, 6, and 7 of this appendix. On the other hand, the selection and content of the quality assurance and quality control activities needed by a monitoring organization depend on a number of local factors such as field and laboratory conditions, the electronic monitoring, the level of data quality needed, the experience of assigned personnel, the cost of control procedures, pollutant concentration levels, etc. Therefore, quality system requirements in section 2 of this appendix are specified in general terms to allow each monitoring organization to develop a quality system that is most efficient and effective for its own circumstances while achieving the data quality objectives required for the SLAMS data.

2. **Quality System Requirements.** A quality system is the means by which an organization manages the quality of its monitoring (information it produces in a systematic, organized manner. It provides a framework for planning, implementing, assessing and reporting work performed by an organization and for carrying out required quality assurance and quality control activities.

2.1. **Quality Management Plans and Quality Assurance Project Plans.** All monitoring organizations must develop a quality system that is described and approved in a quality management plan (QMP) and quality assurance project plan (QAPP) to ensure that the monitoring results:

- Meet a well-defined need, use, or purpose;
- Provide data of adequate quality for the intended monitoring objective;
- Be statistically valid for operations;
- Comply with applicable standards specifications;
- Comply with statutory (and other) requirements of society; and
- Reflect consideration of cost and workload.

2.1.1. The QMP describes the quality system in terms of the organizational structure, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, assessing and reporting activities involving environmental data operations (EDA). The QMP must be readily documented in accordance with EPA requirements in section 2 of this appendix, and approved by the appropriate Regional Administrator, or Regional Administrator's designee. The quality system will be reviewed during the system and/or described in section 2B of this appendix. Organizations that implement the pollution monitoring programs with EPA funds should have a separate QMP document. Similar requirements or organizations that do not implement work with EPA funds may combine the QMP with the QAPP based on negotiations with the funding agency. All internal policies on this process may be found in reference 18 of this appendix. Approved of the recipient QMP by the appropriate Regional Administrator, or the

Regional Administrator's designee, may allow delegation of the authority to review and approve QAPP in the recipient, based on adequacy of quality assurance procedures described and documented in the QMP. The QAPP will be reviewed by EPA during system audits or circumstances related to data quality.

2.1.2. The QAPP is a formal document describing, in sufficient detail, the quality system that must be implemented to ensure that the results of work performed will satisfy the stated objectives. The quality assurance policy of the EPA requires every EDO to have written and approved QAPP prior to the start of the EDO. It is the responsibility of the monitoring organization to adhere to this policy. The QAPP must be readily documented in accordance with EPA requirements in section 2 of this appendix.

2.1.3. The monitoring organization's quality system must have adequate resources both in personnel and funding to plan, implement, assess and inspect the achievement of the requirements of this appendix and its approved QAPP.

2.1.4. **Independent Quality Assurance.** The monitoring organization must provide for a quality assurance management function, at a level to the control management system of the organization that determines and implements the quality policy defined in a monitoring organization's QMP. Quality management includes strategic planning, financial administration and other systematic planning activities (e.g., planning, implementation, assessing and reporting) pertaining to the quality system. The quality assurance management function must have sufficient technical competence and management authority to conduct independent oversight and assure the implementation of the organization's quality system relative to the Ambient Air Quality Monitoring Program and should be organizationally independent of environmental data generation activities.

2.1.5. **Data Quality Performance Requirements.**

2.1.5.1. **Data Quality Objectives.** Data quality objectives (DQOs) or the results of other systematic planning processes are statements that define the appropriate types of data to collect and specify the acceptable levels of potential decision errors that will be used as a basis for establishing the quality and quantity of data needed to support the objectives of the SLAMS data. DQOs will be developed by EPA to support the primary SLAMS objective for each criteria pollutant. As they are developed they will be added to the applicable DQO table. Over the course of systematic planning processes for PSD or other monitoring will be the responsibility of the monitoring organization. The quality of the environmental data generated from data interpretation can be affected by population uncertainty (spatial or temporal uncertainty) and measurement uncertainty (uncertainty associated with collecting, analyzing, reducing and reporting concentration data). This appendix focuses on assessing and controlling measurement uncertainty.

2.1.5.1.1. **Measurement Uncertainty for Automated and Manual PM<sub>10</sub> Methods.** The goal for acceptable measurement uncertainty

is defined as 18 percent coefficient of variation (CV) for total precision and a 20 percent for total bias.

2.1.5.1.2. **Measurement Uncertainty for Automated Ozone Methods.** The goal for acceptable measurement uncertainty is defined for precision as no greater than 30 percent confidence limit for the coefficient of variation (CV) of 7 percent and for bias as an upper 90 percent confidence limit for the absolute bias of 15 percent.

2.1.5.1.3. **National Performance Evaluation Program.** Monitoring plans or QAPP shall provide for the implementation of a program of independent and objective audits of all monitoring providing data for SLAMS and PSD including the provision of a dispute resolution for each audit program. A monitoring plan for QAPP which provides for monitoring organization participation in EPA's National Performance Audit Program (NPAF) and the PM Performance Evaluation Program (PEP) program and which involves the consent of the monitoring organization for EPA to apply an appropriate portion of the grant funds, which EPA would otherwise award to the monitoring organization for monitoring activities, will be deemed by EPA to meet this requirement. For information on its participation, monitoring organizations should contact either the appropriate EPA Regional Quality Assurance (QA) Coordinator or the appropriate EPA Regional Office Director, or the NPAF Coordinator, Pollution Monitoring and Analysis Division (3302-001, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711).

2.1.5.1.4. **Technical Systems Audit Program.** Technical systems audits of each ambient air monitoring organization shall be conducted at least every 5 years by the appropriate EPA Regional Office and reported to the AISC. Systems audit programs are described in reference 10 of this appendix. For further instructions, monitoring organizations should contact the appropriate EPA Regional QA Coordinator.

2.1.5.1.5. **General and Flow Rate Audit Standards.**

2.1.5.1.5.1. **General pollutant concentration measurement performance.** Every air cylinder or compressed gas source, a standard concentration for carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen oxide (NO<sub>x</sub>), and ozone (O<sub>3</sub>) must be traceable to National Institute of Standards and Technology (NIST) Traceable Reference Material (TRM) or a NIST-certified Gas Mixtures and Standards (GMS) certified in accordance with one of the procedures given in reference 4 of this appendix. Vendors advertising certification with the procedures specified in reference 4 of this appendix and distributing gasses as "EPA Protocol Gas" must participate in the EPA Protocol Gas Verification Program or not use "EPA" in any form of advertising.

2.1.5.1.5.2. **Test concentrations for ozone (O<sub>3</sub>).** Test concentrations for ozone (O<sub>3</sub>) must be obtained in accordance with the

Gaseous pollutant concentration standards (permeation devices or cylinders of compressed gas) used to obtain test concentrations for CO, SO<sub>2</sub>, NO, and NO<sub>2</sub> must be traceable to either a National Institute of Standards and Technology (NIST) Traceable Reference Material (NTRM) or a NIST-certified Gas Manufacturer's Internal Standard (GMIS), certified in accordance with one of the procedures given in reference 4 of this appendix. Vendors advertising certification with the procedures provided in reference 4 of this appendix and distributing gasses as "EPA Protocol Gas" must participate in the EPA Protocol Gas Verification Program or not use "EPA" in any form of advertising.

# Part 72 & 75 (stack)

## 1/24/08

(c) On and after January 1, 2009, a specialty gas producer advertising calibration gas certification with the EPA Traceability Protocol or distributing calibration gases as "EPA Protocol Gas" must participate in the EPA Protocol Gas Verification Program (PGVP) described in Section 2.1.10 of the EPA Traceability Protocol or it cannot use "EPA" in any form of advertising for these products, unless approved by the Administrator. A specialty gas producer not participating in the PGVP may not certify a calibration gas as an EPA Protocol Gas, unless approved by the Administrator.



Thank you !

Questions ?

