U. S. EPA Ambient Air Monitoring

Protocol Gas Verification Program

Implementation Plan

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U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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ACRONYMS AND ABBREVIATIONS

AA-PGVP	Ambient Air Protocol Gas Verification Program
AQS	Air Quality System
CAMD	Clean Air Markets Division
CFR	Code of Federal Regulations
COC	chain-of-custody
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
GMIS	Gas Manufacturer's Internal Standard
ICAC	Institute of Clean Air Companies
NACAA	National Association of Clean Air Agencies
NBS	National Bureau of Standards
NERL	National Exposure Research Laboratory
NIST	National Institute of Standards and Technology
NMi	Netherlands Measurement Institute
NPAP	National Performance Audit Program
NTRM	NIST Traceable Reference Material
OAQPS	Office of Air Quality Planning and Standards
OAP	Office of Atmospheric Programs
ORD	Office of Research and Development
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RAVL	Regional Analytical Verification Laboratory
SOP	standard operating procedure
SRM	Standard Reference Material

1.0 INTRODUCTION

1.1 Background and Program Goals

The basic principles of the U.S. Environmental Protection Agency (EPA) *Traceability Protocol for the Assay and Certification of Gaseous Calibration Standards* (EPA, 1997) were developed jointly by EPA, the National Bureau of Standards (now National Institute of Standards and Technology [NIST]), and specialty gas producers over 30 years ago (Scott Environmental Technology, 1977a and b). At the time, commercially-prepared calibration gases were perceived as being too inaccurate and too unstable for use in calibrations and audits of continuous source emission monitors and ambient air quality monitors (Decker et al., 1981). The protocol was developed to improve their quality by establishing their traceability to NIST Standard Reference Materials (SRMs) and to provide reasonably priced products. This protocol established the gas metrological procedures for measurement and certification of these calibration gases for EPA's Acid Rain Program under 40 Code of Federal Regulations (CFR) Part 75, for the Ambient Air Quality Monitoring Program under 40 CFR Part 58, and for the Source Testing Program under 40 CFR Parts 60, 61, and 68. EPA required monitoring organizations implementing these programs ("the regulated community") to use EPA Protocol Gases as their calibration gases.

The protocol has never specified that EPA Protocol Gases would have any given uncertainty and it has never established acceptance criteria for the uncertainty. In 1997, EPA revised the protocol to establish detailed statistical procedures for estimating the total uncertainty of these gases. The total uncertainty can be less that +/- 2.0 percent relative, which is the acceptance criterion that is required for EPA's Acid Rain Program (EPA, 1993).

Specialty gas producers prepare and analyze EPA Protocol Gases without direct governmental oversight. EPA chooses to assure the quality of these gases by conducting independent accuracy assessments of representative gases that are sold by the producers as part of their routine production. In the 1980s and 1990s, EPA conducted a series of EPA-funded accuracy assessments of EPA Protocol Gases sold by producers (Wright et al., 1987 and 1989, Coppedge et al., 1992, Hines et al., 1992 and 1993, Shores et al., 1994). The intent of these audits was to:

- increase the acceptance and use of EPA Protocol Gases as calibration gases;
- provide a quality assurance (QA) check for the producers of these gases; and
- help users identify producers who can consistently provide accurately certified gases.

Either directly or through third parties, EPA procured EPA Protocol Gases from the producers, assessed the accuracy of the gases' certified concentrations through independent analyses, and inspected the accompanying certificates of analysis for completeness and accuracy. The producers were not aware that EPA had procured the gases for these audits.

The accuracy of the EPA Protocol Gases' certified concentrations was assessed using SRMs as the analytical reference standards. If the difference between the audit's measured concentration and the producer's certified concentration was more than +/- 2.0 percent or if the documentation was incomplete or inaccurate, EPA notified the producer to resolve and correct the problem.

The results of the accuracy assessments were published in peer-reviewed journals and were posted on EPA's Technology Transfer Network website[1].

The accuracy assessments were discontinued in 1998. In 2002, there was interest by the specialty gas producers and EPA to reestablish this program. EPA-OAQPS and EPA Region's 7 and 2 are working together to develop an Ambient Air Protocol Gas Verification Program (AA-PGVP). This program is expected to:

- ensure that producers selling EPA Protocol Gases participate in the AA-PGVP and
- provide end users with information about participating producers and verification results.

The EPA Ambient Air Quality Monitoring Program's QA requirements 40 CFR Part 58, Appendix A require:

> *2.6 Gaseous and Flow Rate Audit Standards. Gaseous pollutant concentration standards (permeation devices or cylinders of compressed gas) used to obtain test concentrations for CO, SO_2, NO, and NO_2 must be traceable to either a National Institute of Standards and Technology (NIST) Traceable Reference Material (NTRM), NIST Standard Reference Materials (SRM) and Netherlands Measurement Institute (NMi) Primary Reference Materials (valid as covered by Joint Declaration of Equivalence) 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 gases as "EPA Protocol Gas" must participate in the EPA Protocol Gas Verification Program or not use "EPA" in any form of advertising.*

These requirements give assurance to end users that all specialty gas producers selling EPA Protocol Gases are participants in a program that provides an independent assessment of the accuracy of their gases' certified concentrations. The participating producers will be contacted by EPA when the Region 2 or 7 analytical verification laboratory (RAVL) has measured their gases and they may expect to see the verification results reported in peer-reviewed journals and on EPA website(s).

This program is considered a verification program because its current implementation level does not allow for a large enough sample of EPA Protocol Gases to be measured to yield a statistically rigorous assessment of the accuracy of any producer's gases. It will not provide end users with a scientifically defensible estimate of whether gases of acceptable quality can be purchased from a specific producer. Rather, the results provide information to end users that may inform their purchasing decisions. The final verification results will be reported with an explaining how the results should be interpreted.

Figure 1 provides a comprehensive description of the processes by which the program will be implemented. Important functions are identified by the lines of different colors or line type.

[1] http://www.epa.gov/ttn/

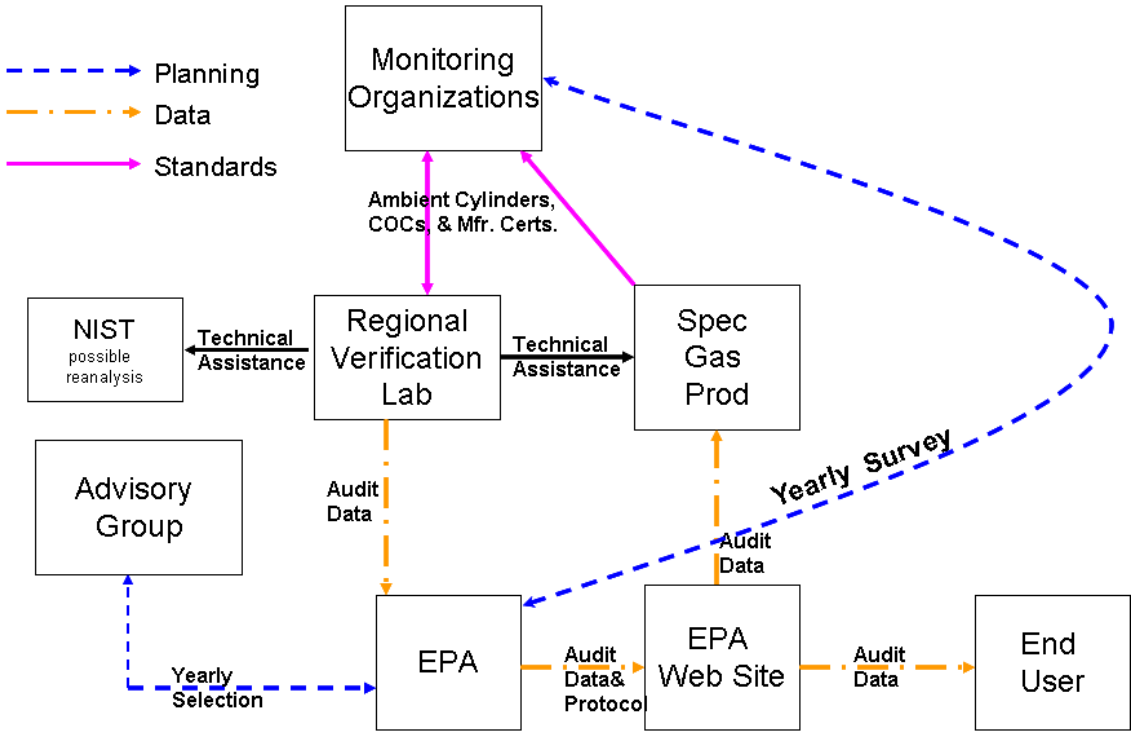

Figure 1 AA-PGVP Flowchart

1.2 Program Summary

Goal

Each year, EPA will attempt to compare gas cylinders from every specialty gas supplier being used by ambient air monitoring organizations. Regions 2 and 7 have agreed to provide analytical services for verifications of 40 cylinders/lab or 80 cylinders total/year. Cylinders will be verified at a pre-determined time each quarter.

Yearly Selection

A Protocol Gas Advisory Group composed of OAQPS, NACAA, a tribal representative from the Tribal Air Monitoring Support (TAMS) Center Steering Committee and Region 2 and 7 will decide the number, composition and concentration of the EPA Protocol Gases that will be verified in a given year. The selection goal in the following order would be:

1) Minimum one gas standard from every specialty gas vendor being used by the monitoring community
2) Selection of a minimum of 3 standards per specialty gas vendor
3) Weight additional standards by vendor market share in ambient air monitoring community

Achievement of the goals is based on willing participation of the monitoring organizations and how many of those organizations are using a particular specialty gas producer.

Analysis

The verification laboratories will set up a 2-3 week period each calendar quarter for cylinder verification analysis. Generally it is assumed that the analysis would be scheduled around the end of each quarter. Monitoring organizations would work with EPA each quarter in order to get the appropriate cylinders sent to EPA in time for the analysis. The analytical in the form of standard operating procedures and a quality assurance project plan have been developed and are posted on the AA-PGVP Website[2].

Funding

Federal Funding --

OAQPS will cover the majority of the costs for the AA-PGVP. Costs will cover the purchase of standard reference materials (SRMs), cylinder shipping from the RAVLs, and equipment/consumables as necessary. EPA will also attempt to cover the costs for training and certification for shipping hazardous materials under 49 CFR Part 172.704

Monitoring Organizations—

In order to maintain the "blind" nature of the AA-PGVP, EPA will receive cylinders from the monitoring organizations after they have purchased them from the specialty gas producers. Monitoring organizations participating in the program will be expected to fund the shipping/transporting of the gaseous standards from their monitoring facility to the Region 2 or 7 RAVL. EPA will cover the costs of shipping cylinders back to the appropriate monitoring organization.

> **NOTE:** In order to ship cylinders to EPA, monitoring organizations will need to trained/certified for shipping have hazardous materials under 49 CFR Part 172.704

Verification Results

The RAVL will provide results from its analyses of the gases and will determine the uncertainty between its measured concentration and the producers' certified concentration (tag value) as described in the *Protocol Gas Document.* This information, once validated, will be sent to OAQPS which will directly notify the specialty gas producers, the monitoring organization providing the cylinder, and will indirectly notify all interested parties by posting the verification results on the AA-PGVP website.

[2] http://www.epa.gov/ttn/amtic/aapgvp.html

Protocol Revisions

EPA, in consultation with the producers, will assess the need to revise the *Protocol Gas Document* from time to time and will revise this document as deemed necessary. These revisions will ensure that the protocol includes any new gas metrological techniques and statistical analysis procedures.

Technical Assistance

The RAVL may need to communicate with the participating producers in order to determine how specific EPA Protocol Gases were prepared or certified. OAQPS will initiate and be included in any communication needed with participating producers.

1.3 Purpose of This Document

The purpose of this document is to provide the necessary technical, logistical, and administrative information to successfully implement the program. The specific purposes include identifying:

- each phase of the program and explaining how it will be implemented;
- roles and responsibilities of all participating organizations;
- specific lines of communication between and among all participants and stakeholders;
- pertinent milestones;
- resources required for successful implementation;
- the logistical elements;
- QA and quality control (QC) procedures; and
- reporting components.

Once this document has been finalized, all participants are expected to implement the program as set forth in this document unless there is a consensus decision by the AA-PGVP Advisory Group that changes are required. The AA-PGVP Advisory Group is responsible reviewing this document from time to time and for making any subsequent changes to this program.

2.0 ROLES AND RESPONSIBILITIES

See Figure 1 for a graphic representation of the relationships between and among the various AA-PGVP stakeholders.

2.1 AA-PGVP Advisory Group

The AA-PGVP Advisory Group consists of representatives from OAQPS, the National Association of Clean Air Agencies (NACAA), the Tribal Air Monitoring Support (TAMS) Center Steering Committee and EPA Region 2 and 7 management and laboratory staff and is responsible for facilitating and coordinating communications and agreements among the various stakeholder organizations (e.g., monitoring organizations or specialty gas producers) involved in the AA-PGVP.

The AA-PGVP Advisory Group is responsible for reviewing this document from time to time and for making any needed changes to this program.

The AA-PGVP Advisory Group is responsible for assisting in the selection of the EPA Protocol Gases to be verified. It will come to a consensus decision via meetings, teleconferences, and/or e-mails as appropriate.

The AA-PGVP Advisory Group is responsible for the development of the verification reports (see Section 6)

2.2 National Association of Clean Air Agencies (NACAA)

NAACA is responsible for selecting a representative to the AA-PGVP Advisory Group to serve for a defined term. The NACAA representative is responsible for appropriate communication about the AA-PGVP with the members of that organization and assisting in promoting participation in the program among the monitoring community (including Tribal monitoring organizations).

NAACA will help implement an annual survey of all specialty gas producers providing gaseous standards to the monitoring organizations. From this list, the AA-PGVP Advisory Group will select cylinders that cover all specialty gas producers and identify the monitoring organizations willing to participate in the PVGP.

2.3 Tribal Air Monitoring Support (TAMS) Center Steering Committee

The mission of the TAMS is to develop tribal capacity to asses, understand and prevent environmental impacts that adversely affect health, culture, and natural resources. Fundamental to the TAMS mission is technical training of tribal professionals and technical assistance in air quality measurements. The TAMS Steering Committee is responsible for selecting a representative to the AA-PGVP Advisory Group to serve for a defined term. The TAMS representative is responsible for appropriate communication about the AA-PGVP and assisting in promoting participation in the program among the tribal monitoring community

2.4 EPA Office of Air Quality Planning and Standards (OAQPS)

OAQPS has overall technical oversight responsibilities for the AA-PGVP. It has the responsibility for disseminating information about the program and verification results to other government entities, producers, the regulated community, other interested parties, and the general public.

OAQPS is responsible for forming the AA-PGVP Advisory Group. It is responsible for identifying representatives of government, and the ambient air monitoring community who can serve in the group. The EPA point of contact will coordinate a yearly conference call/meeting of the AA-PGVP Advisory Group in which the number, composition, and concentration of the EPA Protocol Gases to be verified will be selected. The EPA point of contact will be identified on appropriate EPA websites. The EPA point of contact will also coordinate quarterly conference calls to discuss program progress and issues.

A unique identification number will be assigned by EPA to each manufacturing location that participates in the program. The unique identification number may be used by EPA's National Performance Audit Program (NPAP) when it performs audits of ambient air monitoring organizations and may be used in reporting this data to AQS.

Upon receipt from the AA-PGVP Advisory Group the list of cylinders and their producers for the current year, OAQPS is responsible for publishing and disseminating a list of the participating manufacturing locations and the associated identification numbers on the AA-PGVP website so that all end users can identify which manufacturing locations are participants in the program and so that they can record the identification numbers in their monitoring records as needed.

OAQPS is responsible for notifying each participating producer about whether that producer's certified concentrations (tag value) and the RAVL's corresponding calculated measured concentrations for a specific EPA Protocol Gas differ by more than the acceptable value, but it will not disclose the specific values of the measured concentrations to the producer. It will notify each producer separately. The draft verification results for a producer will not be shared with anyone but that producer. Verification results will include time and date of the verifications and the analyzers used in the test as well as any supporting information (e.g. QC results) needed by the producer.

OAQPS is responsible for publishing and disseminating the final verification results with appropriate caveats and the certificate inspection results by posting them on an EPA website that is accessible to the public. Any producer-reanalyzed concentrations will be posted by EPA in a separate column of the final verification results adjacent to the producers' original certified concentrations with a footnote indicating which manufacturing location performed the reanalysis. EPA will send the final verification results directly to the AA-PGVP Advisory Group, and the participating producers. It may prepare papers concerning the verification results for presentation at professional meetings and for publication in the professional literature.

OAQPS is responsible for establishing and maintaining the archives of all AA-PGVP verifications. OAQPS will determine whether AQS can accept this information.

OAQPS is responsible for preparing a quality assurance project plan (QAPP) for its respective portion of the AA-PGVP. The QAPP will conform to *EPA Requirements for Quality Assurance Project Plans*[3] (EPA, 2001). This document will be submitted to the AA-PGVP Advisory Group for comment and EPA OAQPS and Regional verification laboratories for joint review and approval.

OAQPS is responsible for establishing tracking and chain of custody procedures for shipment of EPA Protocol Gases to and from monitoring organizations.

2.5 Region 2 and 7 Regional Analytical Verification Laboratories

The RAVL are responsible for negotiating resource needs with OAQPS, to accept and log gaseous cylinders arriving at the lab, analyze these cylinders within 3 weeks of receipt, report the verification results and certificate inspection results to OAQPS, and to ship these gases back to the monitoring organizations.

To ensure the validity of the verification, the monitoring organizations gaseous standards must be delivered to the laboratory in the same condition as when they were delivered to the monitoring organizations. The AA-PGVP must be able to document that the gases are delivered to the laboratory without being altered in any manner. Any use of or tampering with the gases prior to their measurement would render the verification results as questionable. The RAVLs are responsible for the receipt and custody of EPA Protocol Gases received from monitoring organizations using the chain of custody form in Appendix B and entering the appropriate fields into the AA-PGVP Database. It is responsible for quarantining these gases securely to prevent tampering until they are measured. The laboratory is responsible for communications associated with receipt and custody of EPA Protocol Gases from the monitoring organizations.

The RAVL are responsible for preparing a QAPP for its respective portion of the AA-PGVP. The QAPP will conform to *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001). The laboratory's QAPP will contain a description of its plan for attaining its project objectives, project organization, chain-of-custody procedures, the analytical instrumentation, the gas metrological techniques, the analytical reference standards, laboratory record-keeping procedures, and the mathematical and statistical procedures that were used in the calculation of the measured concentrations and their estimated total uncertainties as described in Appendix B of the *Protocol Gas Document*. The QAPP will be submitted to EPA for review and approval.

The RAVL is responsible for determining the composition and concentration of EPA Protocol Gases that are sent from the monitoring organizations. It will use analytical instrumentation and gas metrological procedures that are interference-free and NIST standard reference material (SRM) for its analyses of these gases. It will calculate the difference between its' measured concentration and the specialty gas producer's certified concentrations for these gases and

[3] http://www.epa.gov/quality1/qa_docs.html

estimate total uncertainty using accepted and documented statistical techniques. The laboratories will operate all year round but will set up a schedule each quarter for analysis.

The RAVL is responsible for inspecting the EPA Protocol Gases' certificates of analysis to determine their conformance with the documentation requirements of the EPA traceability protocol, including verification of the NTRM or SRM numbers used in the analysis against the NIST inventory of these standards. If a GMIS is used in the analysis, it's traceability to NIST must be indicated on the certificate of analysis. This information will be included in the AA-PGVP database.

Upon completion of its measurements, the RAVL will prepare draft verification results (see Section 6.2) for OAQPS and monitoring organization review.

Upon completion of its analyses and the resolution of any verification-related issues, the RAVL will ship the EPA Protocol Gases using chain of custody procedures back to the monitoring organization. The RAVL will be responsible for the cost of these shipments.

2.6 Monitoring Organizations

The monitoring organizations that are conducting monitoring under 40 CFR Parts 58 are responsible for purchasing EPA Protocol Gases only from those specialty gas producers who participate in the AA-PGVP. Their monitoring documentation will include the manufacturing location's unique identification number.

Each year monitoring organizations will complete the AA-PGVP Monitoring Organization Survey. The survey will is used to identify the specialty gas producers used by the monitoring, whether it plans to purchase protocol gas in the upcoming calendar year and whether it would like to be an active participant in the program (shipping cylinders for verification).

The participating monitoring organizations will be placed on a list that includes the approximate timeframe of cylinder purchase and will be required to notify the RAVL one month prior to the monitoring organizations receipt of cylinder in order to set up a reasonable timeframe for the laboratory to set up a verification schedule. It is anticipated that the labs will set up a quarterly analysis schedule. Therefore, the monitoring organizations must work within that schedule and in general be able to have the protocol gas cylinder be at the verification lab for a maximum of 6 weeks.

The monitoring organizations will send a chain of custody form (see Appendix B), the stamped cylinder numbers, the composition, the certified concentrations and certified cylinder pressures to the RAVL. This information will be used by the laboratory to help to ensure that it receives and analyzes all the gases that are intended to be verified and no others.

The monitoring organizations will notify the RAVL the day that the protocol gases are shipped. The gases must be delivered with the same internal pressure as indicated on their certificates of analysis. They must have at least 6 months left in their certification periods.

As mentioned is Section 1, in order to ship cylinders to EPA, monitoring organizations will need to be trained/certified for shipping have hazardous materials under 49 CFR Part 172.704. As part of the participation survey, EPA will ask monitoring organization whether they have this training certificate on the Survey. For those who do not but would like to participate in the AA-PGVP, EPA will attempt to provide on-line or web based training seminars for this certification requirement.

Monitoring organizations will receive results of verifications within 3 weeks of the analysis. If results are outside the acceptance windows, the analytical lab will attempt to verify/ensure that its analytical activities were appropriate (see QA Section). The RAVL will work with the monitoring organization on other reasonable trouble shooting techniques but it is not responsible for any specific corrective action. The monitoring organizations will be responsible for determining further corrective action steps once cylinders are sent back to the monitoring organizations.

Primary Quality Assurance Organizations and Reporting Organizations—

For QA purposes, EPA defines the primary quality assurance organization (PQAO) as a monitoring organization or a coordinated aggregation of such organizations that is responsible for a set of stations that monitors the same pollutant and for which data quality assessments can logically be pooled. Each criteria pollutant sampler/monitor at a monitoring station in the SLAMS network must be associated with one, and only one, primary quality assurance organization. However, there are a number of local monitoring organizations that have consolidated to fewer PQAOs. These monitoring organizations may use different gaseous standards even though they are associated with the same PQAO. EPA will survey participation in the AA-PGVP at the PQAO level. It will be the responsibility of the PQAO to survey the monitoring organizations within the PQAO.

2.7 U. S. Environmental Protection Agency (EPA) Office of Research and Development (ORD)

ORDs Air Pollution Prevention and Control Division (APPCD) within the National Risk Management Research Laboratory, in consultation with the specialty gas producers, is responsible for revising the *Protocol Gas Document* from time to time to reflect technological advances in gas metrology and statistics. It has the responsibility for publishing the revised protocol and posting it on an appropriate EPA website that is accessible to the public.

2.8 Specialty Gas Producers

Specialty gas producers must prepare and analyze EPA Protocol Gases according to the current version of the *Protocol Gas Document*. The producer's unique identification number for the manufacturing location preparing an EPA Protocol Gas, if one exists, must be included in the certificate of analysis for the gas. If a unique code does not exist EPA will designate codes for each producers manufacturing site.

If a producer has been informed by EPA that the draft verification results for a specific EPA Protocol Gas and the producer’s corresponding certified concentrations differ by more than the

acceptable uncertainty, it may choose to have that gas reanalyzed by its manufacturing location or by another laboratory at its own expense. The producer must report the results of the reanalysis to EPA by February 1 of the year following verification in order to include this information in final reports by March of the year following verification.

There may be cases where, based on the survey results, specialty gas producers will not be used by monitoring organizations for a particular year. In addition, the specialty gas producers may want to provide cylinders for verification as a way of testing the verification process. If resources permit, EPA will try to accommodate these verifications by setting up a specific timeframe when these verifications can be implemented.

3.0 RESOURCES

It is expected that the majority of the resources needed for this program will be covered by internal EPA base QA funding. This section will explain the funding sources, funding mechanisms, and program cost estimates needed to implement the AA-PGVP.

3.1 OAQPS Costs

It is not anticipated that OAQPS will need additional in-house resources for this program. EPA will provide for regional costs through internal base QA funds that support regional activities. EPA will devote 0.15 FTE for the planning year and 0.10 FTE in out years.

3.2 RAVL Costs

Table 3-1 provides an estimate cost to the Region 7 and Region 2 analytical laboratory. This estimate assumes approximately 40 cylinders/lab verified each year.

Table 3-1 Estimated AA-PGVP Costs

Startup Cost:	**Region 7**	**Region 2**	**Comments**
NIST SRM Gas Standards	$9,000	9,000	3 NIST SRM cylinders/lab
Gas Calibrator	$14,500		
Data Logging System	$4,500		
Regulators	$1,000	$1,000	
Miscellaneous Supplies	$2,000	$4,000	
Startup Total	**$31,000**	**$14,000**	
Annual Operating Cost			
Shipping (40X$80)	$3,200	$3,200	
NIST SRM Standard replacement	$9,000	$9,000	
Equipment replacement	$4,500	$4,500	Purchase of new instrument every 3 years
Miscellaneous Supplies	$2,000	$2,000	
Repair parts	$1,000	$1,000	
Annual Operating Cost Total	**$19,700**	**$19,700**	

It is currently anticipated that the analytical verification lab analysis will be implemented by federal employees at an estimate of 0.20 FTE/year/lab.

NIST Standard Reference Materials (SRMs)

The Regional verification laboratories will purchase the NIST SRMs listed in Table 3-2. The verification laboratories will work with NIST at appropriate timeframes to ensure an uninterrupted supply of SRMs are available for the program.

Table 3-2 NIST SRMs used in AA-PGVP

Analyte	**SRM Number**	**Concentration**	**SRM Number**	**Concentration**
CO	SRM 2639a	10,000 ppm	SRM 2637a	2500 ppm
NO	SRM 1683b	50 ppm	SRM 1684b	100 ppm
SO2	SRM 1693a	50 ppm	SRM 1694a	100 ppm

4.0 LOGISTICS

The AA-PGVP objective, from a logistics standpoint, involves shipping the EPA Protocol Gases from the producers to the monitoring organizations, from the monitoring organizations to the RAVL, and finally the RAVL shipping the standards back to the monitoring organizations.

4.1 Acquisition of Protocol Gases

The monitoring organizations are responsible for purchasing of EPA Protocol Gases to be analyzed by the RAVL. The goal of the AA-PGVP is to ensure that the acquisition of the protocol gas from the specialty gas producer appears as a routine purchase and is the reason the monitoring organizations will purchase the cylinders and ship them new and unused to the RAVL.

The RAVL will purchase NIST SRM standards to be used for the verification process. Dates of certifications and recertification will be included in the AA-PGVP database.

4.2 Shipments of EPA Protocol Gases to RAVL

RAVL Identification

Since 2 laboratories (Regions 2 and 7) will participate in the program, during the annual planning activity, the participating monitoring organizations will be identified with a particular RAVL. The pairing will most likely be made by geographic location but the pairing may be based on types and concentrations of standards needing certifications and the SRMs at a particular RAVL.

Verification Scheduling

Each calendar quarter, a two or three week window will be identified for the cylinder verifications. Initial scheduling of a monitoring organization for a particular quarter will be based on the annual monitoring organization survey which includes information on when a monitoring organization participant plans to purchase protocol gasses. The RAVL will contact the monitoring organization at the beginning of each quarter to determine if they still plan on purchasing protocol gasses within that quarter and participating in the verification. If so, the monitoring organization will be confirmed for verification and information in regards to the actual verification schedule and when cylinders should be sent to the EPA Region will be distributed to the monitoring organization participants.

Protocol Gas Shipments from Monitoring Organizations to Verification Laboratories

The EPA Protocol Gases, its associated certificates of analysis and the chain of custody will be shipped directly from the monitoring organizations to the RAVL. Monitoring organizations are responsible for the cost of shipping the gases to the laboratory. The monitoring organization will notify the RAVL minimally one week ahead of the expected shipping day and the actual day of shipment. Contact can be voice or email but must include the shipping tracking number in order

for tracking by the RAVL. The gases must be delivered with the same internal pressure as received from the producers and must have at least 6 months left in its certification periods. The RAVL will inform the monitoring organization of receipt of cylinders/information the day the cylinder arrives.

Chain of Custody and Tracking of Shipments

The monitoring organizations will initiate a chain of custody record (see Appendix B) for cylinder shipments to the RAVL. This information will be used by the laboratory to ensure that it receives and analyzes all the gases that are intended to be verified and will be used to develop the AA-PGVP database.

4.3 Shipments of EPA Protocol Gases to the Monitoring Organization

Upon completion of its analyses and the resolution of any verification-related issues, the RAVL will ship the EPA Protocol Gases, final results and the completed chain of custody form back to the monitoring organization. The RAVL is responsible for the cost of the return shipment. EPA Regions will have the appropriate safety training for handling/shipping of hazardous materials as required by 49 CFR Part 172.704.

5.0 QUALITY SYSTEM DEVELOPMENT

This section addresses the quality assurance (QA) and quality control (QC) activities for the processes and resulting products in the AA-PGVP. Because the purpose of the program is to assess the accuracy of the EPA Protocol Gases' certified concentration, it is important to also determine how well the program's QA and QC activities have been performed. These activities are performed to assure stakeholders that the program's results can be trusted. They include the activities as described below. They should be carried out according to each organization's documented quality system.

5.1 The AA-PGVP Quality Assurance Project Plan and SOPs

The complete details of the AA-PGVP quality system will be detailed in the AA-PGVP Quality Assurance Project Plan. Due to the importance of the data and its use, EPA identifies this as a category 1 (most stringent) QAPP and as such, will address all QAPP elements that are relevant to the AA-PGVP. This document will be reviewed and approved prior to implementation of the formal program.

The SOPs at a minimum will cover the requirements in procedure G-1 and G-2 of the EPA Protocol Gas Document. In most cases procedure G-2 will be used. The RAVLs will follow the G-1/G-2 requirement but be more specific in the SOPs as they relate to the labs particular instrumentation.

5.2 Quality Control (QC) Activities

There are basically three facets of the program that are important to control: cylinder integrity, cylinder analysis and information collection/assessment/reporting. Each will briefly be discussed below. More detail on quality assurance activities will be covered in the AA-PGVP QAPP.

5.2.1 Cylinder Integrity

To ensure the validity of the verification, the gases must be delivered to the laboratory in the same condition as when they were delivered to the monitoring organization. Any use of or tampering with the gases prior to their measurement would render the verification results as questionable. Cylinders must be handled in such a manner that there integrity is beyond question. Handling includes maintenance from: shipping to the RAVL, laboratory storage, the verification process, and shipping back to the monitoring organization. The QAPP will provide detailed requirements for each phase. Maintaining and documenting the chain of custody for the EPA Protocol Gases being verified is an important responsibility for the RAVL. The monitoring organization will send the important cylinder information as described in Section 4.2 and Appendix B to the RAVL. This information will be used by the laboratory to help to ensure that it receives and analyzes all the gases that are intended to be verified and no others. The RAVL will store cylinders in a secure laboratory location with limited access and by all EPA laboratory safety standards. Upon completion of analysis, the RAVL will complete appropriate section of the chain of custody form which will accompany the cylinder and verification results that are sent back to the monitoring organizations.

5.2.2 Cylinder Verification (Analysis)

The RAVL will be responsible for establishing and implementing internal QC procedures for the measurement of the EPA Protocol Gases, along with associated documentation such as:

- SOPs, laboratory notebooks and maintenance records
- Analytical and support equipment selected to conduct the analyses
- Calibration and configuration of analytical instruments
- Documentation of the measurements including zeros, spans, linearity checks, time to stable response, interferences, precision, accuracy, specificity
- Written procedures for calculation of measured concentrations
- Estimated total uncertainty of the measured concentrations

Table 5-1 provides some of the QC checks that will be included in the QAPP for this program.

Table 5-1 QA AA-PGVP QC Checks

Requirement	Frequency	Acceptance Criteria	Protocol Gas Doc. Reference	Comments
Completeness	All standards analyzed	95%		The goal is based on an anticipated 40 cylinders per lab per year.
Quarterly Flow Calibration	Quarterly -no more than 1 mo. before verification	Calibration flow accuracy within ± 1%	2.3.7	Using flow primary standard
Calibrator Dilution Check	Quarterly -within 2 weeks of assay	± 1% RD	2.3.5.1	Second SRM. Three or more discrete measurements
Analyzer Calibration	Quarterly - within 2 weeks of assay	± 1% RPD (each point) Slope 0.89 – 1.02	2.1.7.2	5 points between 50-90% of upper range limit of analyzer + zero point
Zero & Span Verifications	Each day of verification	SE mean ≤ 1% and accuracy ± 5% RD	2.1.7.3 , 2.3.5.4	Drift accountability. 3 discrete measurements of zero and span
Precision Test [1]	Day of Verification	± 1% RD standard error of the mean	2.3.5.4	SRM at conc. >80% of analyzer URL
Routine Data Check	Any Standard with Value >2% Tag Value	NA		Sample run three times to verify value.
Lab Comparability	2/year	± 2 % RPD	NA	Sample run three average value used.
Standards Certification				
Primary flow standard	Annually-Certified by NVLAP certified lab	1.0 %	**NA**	Compared to NIST Traceable
NIST SRMs	Expiration date SRM pressure > 150 psig			Will follow NIST recertification requirements

5.2.3 Information Collection, Assessment and Management

The following information will be tracked by the RAVL:

- EPA Protocol Gases received;
- Original producer's certificate of analysis for each gas;
- Chain of custody forms;
- Description of the analytical methods;

- Analytical reference standards used in the measurements;
- Identification of the verified cylinders, their producers, and their certified concentrations;
- Raw measurements and a summary of the measured concentrations for the gases; and
- Comparison of the measured concentrations with the certified concentrations.

The raw data from the analyses of the cylinders and the reference standards will be presented in sufficient detail to allow reconstruction of the calculations. The statistical analysis of the verification results will follow the requirements in appendices A and C of the *Protocol Gas Document*. The report will also describe the mathematical and statistical procedures that were used in the calculation of the measured concentrations and the estimated total uncertainties.

5.3 Other QA Activities

There are a number of quality assurance activities that will be implemented to provide confidence in the results of the AA-PGVP.

5.3.1 Verification Laboratory Personnel Certification

The EPA OAQPS QA Officer will certify personnel who are capable of performing the AA-PGVP cylinder verifications. Certification will be established through an audit of the laboratory technician's implementation of the AA-PGVP standard operating procedures. The RAVLs will maintain a listing of these personnel.

5.3.2 Technical System Audits (TSA) and Proficiency Tests (PTs) of RAVL.

OAQPS will invite personnel from the Office of Research and Development (ORD) to perform a TSA on the RAVLs every 3 years. NIST will be invited to review/comment on the AA-PGVP QAPP and SOPs. NIST will also be invited to audit the verification activities and challenge the system with an independent set of proficiency test standards. All results of PTs and TSAs will be posted on an EPA Website.

6.0 INFORMATION MANAGEMENT/ REPORTING

This section will discuss the important AA-PGVP information that needs to be collected, stored and reported. A database will be developed that will collect vital information from a number reports that will be generated throughout the implementation phase of the AA-PGVP.

6.1 Information Needed for AA-PGVP

6.1.1 Identification of AA-PGVP Producers/Participants

The specialty gas producers who will participate in the AA-PGVP each year will be based on: 1) the monitoring organizations use of those specific specialty gas producers and 2) specialty gas producers not currently being used by monitoring organizations that may want to provide cylinders for verification. Each year EPA will survey the monitoring organizations for the following information:

Annual AA-PGVP Participation Survey		
Monitoring organization name	Primary Quality Assurance Organization code	Reporting Organization Code
Monitoring Org Point of Contact (POC)	POC phone #	POC Email
Names of specialty gas producers (SGP) used	SGP address (city, state)	SGP code**
General cylinder concentrations	Anticipated purchase in 12 months	Willingness to participate in AA-PGVP verification

** if there is no code, EPA will establish a coding system for specialty gas producers.

EPA will use AQS to generate a list of all primary quality assurance organizations (PQAOs) that will be used to ensure that all monitoring organizations are surveyed. OAQPS and the EPA Regions will work together to ensure a representative from each PQAO completes the survey by Mid-November of each year. Information from this survey will be the first level of information reported to the AA-PGVP data base. Upon completion of this survey, EPA will report a complete list of **only** the specialty gas producers that are currently being used by monitoring organizations. **This report will not include, at this time, how many monitoring organizations or which monitoring organizations are using specific specialty gas producers.** The list will be useful for specialty gas producers to confirm they are being used by monitoring organizations and if not, to contact EPA if they would like to participate during an agreed upon time period where the specialty gas producers could ship protocol gas directly to the verification labs. Specialty gas producers sending standards directly to EPA will be indentified as such in final reports.

6.1.2 Selected Specialty Gas Producers/Monitoring Organizations

The Pre-implementation survey information will be used to select a representative number of gas cylinders from every specialty gas producer being used for the year. The AA-PGVP data base will identify the subset list of specific specialty gas producer/monitoring organizations that will participate in the upcoming AA-PGVP implementation year. Additional data needed to be collected other than data from the AA-PGVP Pre-implementation survey include:

- Anticipated date for cylinder shipment to verification laboratory
- Anticipated concentration ranges of gases

6.1.3 Chain of Custody Information

Chain of custody is discussed in Section 4 and the chain of custody form can be found in Appendix B. The AA-PGVP data base will capture all information on this form. Many of the variables will be captured/transferred from the AA-PGVP pre-implementation survey information.

6.1.4 Verification Data

The RAVL will capture the following information:

- Standard reference materials (SRM)
    - concentration results,
    - certification date,
    - cylinder ID number
- QC Data (see Table 5-1)
- Monitoring organization standard
    - chain of custody information (Appendix B)
    - concentration results

6.2 Verification Reports

The information described in the above sections will allow for the generation of the following reports:

6.2.1 Initial Draft Report

Within two to three weeks of completion of its analyses, the RAVL will report its draft verification results in the form of a database to OAQPS and the appropriate monitoring organization. At a minimum, the draft verification results shall include:

(a) a description of the gas metrological techniques, analytical method, analytical instrumentation, the statistical procedures that were used in the calculation of the measured concentrations and estimates of total uncertainty;
(b) the analytical reference standards that were used with their compositions, certified concentrations, stamped cylinder numbers and expiration dates;
(c) a description of the EPA Protocol Gases that were analyzed, including their compositions, original certified concentrations and uncertainties, stamped cylinder numbers and expiration dates;
(d) the raw measurement data, measured concentrations, and estimated total uncertainties;
(e) the percent difference between original certified concentrations and calculated measured concentrations;
(f) a documentation checklist for each certificate of analysis with any non-conformances identified;

(g) documentation of whether appropriate chain-of-custody procedures were followed; and
(h) written documentation showing the calculations that the RAVL used to convert the raw measurement data into the measured concentrations and their estimated total uncertainties.

The raw measurement data from the analyses of the EPA Protocol Gases and the analytical reference standards will be presented in sufficient detail to allow reconstruction of the calculations.

OAQPS is responsible for notifying each participating producer about whether the verification results for a specific EPA Protocol Gas that the producer prepared and the producer's corresponding certified concentrations differ by more than 2.0 percent, but it will not indicate the measured concentrations that the laboratory has determined, the direction of the difference (+ or -) or the magnitude. It will notify each producer separately. The draft verification results for a specific producer will not be shared with anyone but that producer and the monitoring organization that sent the standard.

Any disputes about the verification results will be resolved prior to their final dissemination. If a producer has been informed by OAQPS that the measured concentrations for a specific EPA Protocol Gas and the producer's corresponding certified concentrations differ by more than +/- 2.0 percent, then it may choose to have that gas reanalyzed by its manufacturing location or by another laboratory at its own expense. The producer must report the results of the reanalysis to the RAVL who will transmit them to OAQPS with the final verification results.

6.2.2 Final Verification Results

Upon receipt of the final verification results from the RAVL, OAQPS will publish the final verification results (with appropriate caveats associated with how they should be interpreted) and the certificate inspection results by posting them on the EPA AA-PGVP website that is accessible to the public.

The final verification results will include a list of the AA-PGVP participants for that year, the number, composition, and certified concentrations of the EPA Protocol Gases that were verified, summaries of the laboratory's measured concentrations, the estimated total uncertainties, and a comparison of the measured concentrations with the participants' certified concentrations. The reanalyzed concentrations will be posted by EPA in a separate column of the verification results next to the original certified concentrations with a footnote indicating which manufacturing location performed the analysis.

EPA may prepare papers concerning the final verification results for presentation at professional meetings and for publication in the professional literature.

The EPA website will include results from the most recent verification as well as the verification results from previous years.

7.0 ANNUAL AA-PGVP TIMELINE

The purpose of this Section of the AA-PGVP Implementation Plan is to provide the necessary time line sequence for a yearly cycle in the Protocol Gas Verification Program .

Task 1 – Soliciting Participation

Date: Aug –November 1 each year

Party: AA-PGVP Advisory Group

Action: The AA-PGVP Advisory Group will post a survey as described in Appendix A .This information will provide EPA with the information it needs to select a representative number of cylinders from each producer within the constraint of a maximum of 80 cylinders/year.

> **NOTE:** Some of this information will be restricted to the public until verification is completed since gas producers could determine from the list what organizations might be receiving gasses and potentially be used for verifications.

Task 2 – Selection of Producers/Participants.

Date: November 15 each year

Party: AA-PGVP Advisory Group

Action: The AA-PGVP Advisory Group will make selections of producers and participants. From this information EPA will work with selected monitoring organizations to set up a verification implementation schedule based on anticipated purchase dates of cylinders by the selected monitoring organizations.

Task 3 – Participation Finalized

Date: November 30 each year

Party: AA-PGVP Advisory Group

Action: EPA will complete discussions with monitoring organizations and publish a final list that will remain internal to the AA-PGVP Advisory Group until completion of verification for the calendar year. At a minimum, specialty gas producers can be informed whether or not they will have cylinders verified and if not they can determine whether they would like to send cylinders to the verification labs within a window of opportunity offered them.

Task 4 – AA-PGVP Implementation

Date: Jan 1, - December 30, each year

Party: RAVL

Action: The RAVL will implement the routine verification activities and communicate results to OAQPS and monitoring organizations within 5 days of valid analysis.

Task 5 – Official Posting of Results

Date: March 30, each year

Party: EPA

Action: Upon completion of verification and rectification of issues, final results will be posted on AMTIC. Results will include complete lists of surveys and monitoring organization participants. If cylinders are re-verified, these results will also be reported either as final results (if re-verified before Jan. 30) or as an update to the report.

Task 6 – Quarterly AA-PGVP Advisory Group Conference Calls

Date: Quarterly- Starting June 2009

Party: AA-PGVP Advisory Group

Action: The AA-PGVP Advisory Group will meet quarterly to discuss program progress and issues. As experience is gained in the program the AA-PGVP Advisory Group will determine if changes in program documentation (Implementation Plan, QAPP, SOPs) needs modification. These modifications will be made as soon as needed but documented, at a minimum, before the start of the next calendar year.

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9.0

APPENDICIES

Appendix A

AA-PGVP Monitoring Organization Survey

This Survey would be sent to all primary quality assurance organizations (PQAOs) currently submitting SLAMS/SPM/PSD data to AQS. It will provide EPA with information on:

1. Specialty gas producers currently being used, and
2. Monitoring organizations willing to participate in the AA-PGVP

Monitoring organization willing to participate would be required to meet Implementation Plan requirements which include covering the cost of shipping to the Regional Analytical Verification Laboratory and allowing the laboratory to hold the cylinder for approximately 6 weeks.

For QA purposes EPA defines the primary quality assurance organization (PQAO) as a monitoring organization or a coordinated aggregation of such organizations that is responsible for a set of stations that monitors the same pollutant and for which data quality assessments can logically be pooled. Each criteria pollutant sampler/monitor at a monitoring station in the SLAMS network must be associated with one, and only one, primary quality assurance organization. However, there are a number of local reporting organizations that have consolidated to fewer PQAOs. These reporting organizations may use different gaseous standards even though they are associated with the same PQAO. EPA will survey participation in the AA-PGVP at the PQAO level. It will be the responsibility of the PQAO to survey the reporting organizations within the PQAO.

The participation form will be provided in Word and as an Excel spreadsheet. It is expect that each PQAO/Reporting Organization combination would provide a separate form.

AA-PGVP Monitoring Organization Participation Survey

PQAO Organization Name:_____	**PQAO Code:** _____
Reporting Org. Name[1]: _____	**Reporting Org. Code:** _____
Point Of Contact (POC): _____	**POC Email Address:**_____

Specialty Gas Producers Used	**Manufacturer Address**	**Gas Producer Code (if available)**
1) Primary:_____	**City:**_____ **State:** _____	_____
2) Secondary:_____	**City:**_____ **State:** _____	_____
3) Other:_____	**City:**_____ **State:** _____	_____

Do you plan on purchasing gasses from a producer in the next 12 months?	**(Y/N)** ____	**Approximate date of purchase** Month (number): _____

Pollutants you plan to purchase and their concentrations

Pollutant	**Concentration**	**Multi-Blend Y/N**	**Pollutant**	**Concentration**	**Multi-Blend Y/N**

Would you be willing to participate in the PGVP?	**(Y/N)** ____	
Is your Org. trained/ certified to ship gas cylinders[2]?	_____	

[1]-Due to consolidation of PQAOs there may be more than one reporting organization using the same PQAO. EPA is requesting that the "Primary" PQAO provide information on all reporting organizations using the PQAO code. Therefore, if a unique PQAO supports 3 reporting organizations, EPA would expect to receive three survey forms

[2]- Per 49 CFR Part 172.704 Training for shipment of hazardous material

Appendix B - Example AA-PGVP Chain-of-Custody Form

TO BE COMPLETED BY MONITORING ORGANIZATION

Cylinder Information

Monitoring Organization:_____ Point of Contact: _____

Primary Quality Assurance Organization Code :_____

Producer Name: _____ Producer Point of Contact:_____

Manufacturing Location Address: _____

Contact Phone Number: _____ Contact E-Mail:_____

Specialty gas vendor has verified the standard by comparison to: SRM NTRM GMIS (circle one)

Stamped Cylinder #: _____ Pressure _____ psig Certification Expiration Date _____

Constituents	SO2 (ppm)	NO (ppm)	CO2 (%)	O2 (%)	CO (ppm)
Certified Concentration					
Analytical Uncertainty					

Agent Receipt Date: _____ Received By: _____

Date Shipped to Laboratory: _____ Shipping Mode & Carrier:_____

Shipping Tracking #: _____

Send this COC form with cylinder, and email form to the laboratory.

TO BE COMPLETED BY RAVL

Upon Receipt:
Laboratory Receipt Date: _____ Received by: _____

Integrity Acceptable: Yes ____ No____ Contents Information Correct: Yes____ No____

Cylinder valve shrink wrapped: Yes_____No____ CGA shrink wrap is intact: Yes_____ No_____

Certification Expiration Date: _____ Confirm cylinder pressure: _____ psig

Shipping to Monitoring Organization:

Confirm cylinder pressure: _____ psig (post verification)

Date Shipped to Monitoring Org: _____ Shipping Mode & Carrier: _____

Shipping Tracking #: _____

Send this COC form to EPA upon completion of the measurements and resolution of all verification-related issues

Appendix C
Protocol Gas Verification Cylinder Tracking Form

The following information will be automatically assembled from the AA-PGVP Data Base as data is entered from the chain of custody forms and undergoes verification. It will then be posted in a manner (AMTIC) that will be available to the monitoring organizations.

PQAO	Cylinder ID	Date Shipped From MO	Date Received By Lab	Date Verified	Date Shipped back to MO