United States Environmental Protection Agency	Office of Air Quality Planning and Standards Research Triangle Park, NC 27711	EPA March, 2010
Air		

Quality Assurance Document

Quality Assurance Project Plan for the Ambient Air Protocol Gas Verification Program

Foreword

U.S. Environmental Protection Agency (EPA) policy requires that all projects involving the generation, acquisition, and use of environmental data be planned and documented and have an Agency-approved Quality Assurance Project Plan (QAPP) before the start of data collection. The primary purpose of the QAPP is to provide a project overview, describe the need for the measurements, and define quality assurance/quality control (QA/QC) activities to be applied to the project, all within a single document.

The following document represents the QAPP for the environmental data operations involved in EPA's Ambient Air Protocol Gas Verification Program (AA-PGVP). This QAPP was generated using the following EPA monitoring and QA regulations and guidance:

- 40 CFR Part 58 Appendix A and C
- *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans*
- *EPA QA/G-5, Guidance for Quality Assurance Project Plans*.

All pertinent elements of the QAPP regulations and guidance are addressed in this QAPP.

This document has been reviewed by EPA Region 2 and 7 personnel responsible for implementing the PGVP in their respective Regions and is considered acceptable (see the following approval page).

Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use.

Acknowledgments

This Quality Assurance Project Plan (QAPP) is the product of the combined efforts of the U.S. Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards (OAQPS); and the EPA Regional Offices. The review of the material in this document was accomplished through the activities of the PGVP Advisory Group. The following individuals are acknowledged for their contributions.

EPA Regions

Region

2	Avraham Teitz, Mustafa Mustafa
7	Thien Bui and James Regehr

Moinitoring Organizations

Brenda Jarrell-Southern Ute Indian Tribe

George Froelich- NY Department of Environmental Protection

Office of Reserach and Development

Robert Wright

Office of Air Quality Planning and Standards

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Mike Papp

Acronyms and Abbreviations

AA-PGVP	Ambient Air Protocol Gas Verification Program
AQS	Air Quality System
CAA	Clean Air Act
CFR	Code of Federal Regulations
COC	chain of custody
DQA	data quality assessment
DQOs	data quality objectives
EDO	environmental data operation
EPA	Environmental Protection Agency
FEM	Federal equivalent method
FIPS	Federal Information Processing Standards
FRM	Federal reference method
GMIS	(NIST- Certified) Gas Manufacturer’s Internal Standard
LAN	local area network
MDW	measurement data worksheet
MQOs	measurement quality objectives
NAACA	National Association of Clean Air Agencies
NAAQS	National Ambient Air Quality Standards
NIST	National Institute of Standards and Technology
NTRM	(NIST) Traceable Reference Material
OAQPS	Office of Air Quality Planning and Standards
OARM	Office of Administration and Resources Management
ORD	Office of Research and Development
PC	personal computer
PD	percent difference
PE	performance evaluation
QA/QC	quality assurance/quality control
QA	quality assurance
QAM	Quality Assurance Manager
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QMP	Quality Management Plan
RAVL	Regional Analytical Verification Laboratory
RD	relative difference
RPD	relative percent difference
SLAMS	state and local monitoring stations
SOP	standard operating procedure
SOW	statement of work
TAMS	Tribal Air Monitoring Services
TSA	technical system audit
TSP	total suspended particulate
V_a	air volume, at ambient or actual conditions
WAM	Work Assignment Manager

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1.0 QA Project Plan Identification and Approval

Title: Ambient Air Protocol Gas Verification Program Quality Assurance Project Plan

Category: 1

The attached Quality Assurance Project Plan (QAPP) for the Ambient Air Protocol Gas Verification Program (AA-PGVP) is hereby recommended for approval and commits the participants of the program to follow the elements described within.

Signature: Michael Papp **Date:** 4/2/10

Mike Papp
QA Lead Ambient Air Monitoring Program
Office of Air Quality Planning and Standards

Signature: Avraham Teitz **Date:** 4/12/10

Region 2 Avraham Teitz, RAVL Lead

Signature: Th Bui **Date:** 4/14/10

Region 7 Thien Bui, RAVL Lead

Signature: Joe Elkins **Date:** 4/5/10

Joe Elkins
QA Manager Office of Air Quality Planning and Standards

2.0 Table of Contents

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3.0 Distribution

A copy of this QAPP will be distributed to the AA-PGVP Leads in OAQPS, Regions 2 and 7 and to the AA-PGVP Advisory Group.

OAQPS Leads- Mike Papp, Dennis Crumpler, Mark Shanis

OAQPS QA Manager- Joe Elkins

Region 2- Avraham Teitz, Mustafa Mustafa

Region 7- Thien Bui, James Regehr

AA-PGVP Advisory Group- Brenda Jarrel, George Froelich

If any personnel besides the personnel listed in Region 2 and 7 above implement the program, they will be trained by the personnel currently listed above on the standard operating procedure (SOPs), provided a copy of this QAPP and expected to adhere to the requirements within. Trained personnel will be documented in the AA-PGVP files. A copy of this document will be made available on AMTIC[1]. The document will be reviewed annually and updated as needed.

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

4.0 Project/Task Organization

See Figure 4.1 for a graphic representation of the relationships between and among the various AA-PGVP stakeholders. This section will describe how the AA-PGVP is organized and the roles of the various parties.

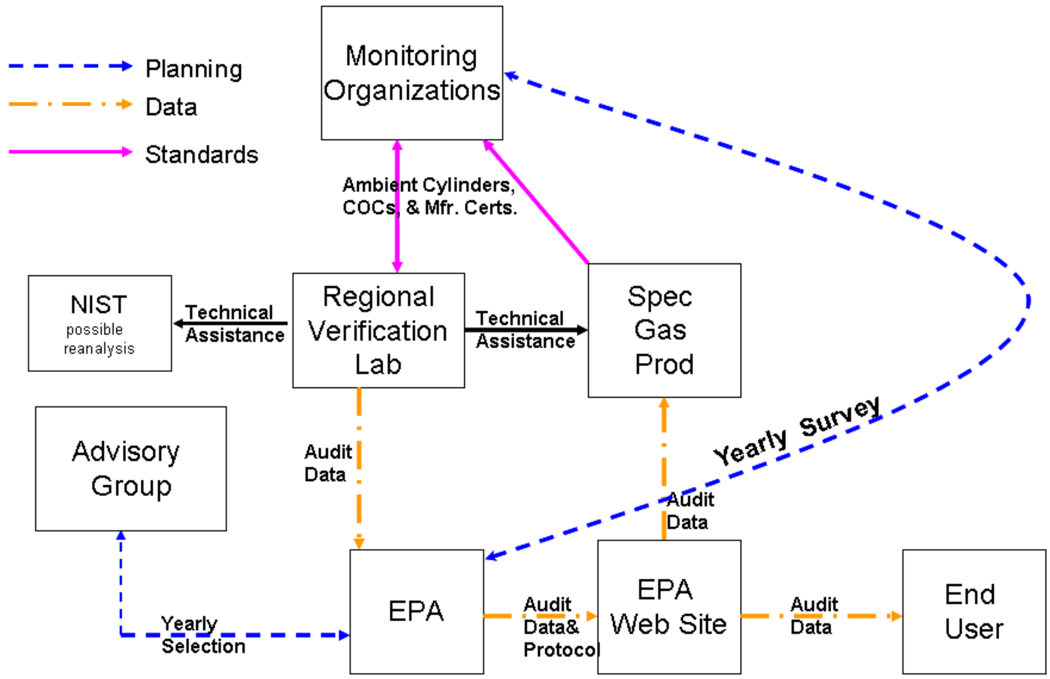

Figure 4.1 AA-PGVP Flowchart

4.1 AA-PGVP Advisory Group

The AA-PGVP Advisory Group consists of representatives from EPA OAQPS, National Association of Clean Air Agencies (NACAA), Tribal Air Monitoring Support (TAMS) Center Steering Committee and EPA Regions 7 and 2 management and laboratory staff. The Advisory Group is responsible for facilitating and coordinating communications and agreements among the various stakeholder organizations (e.g., 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 selecting, on a yearly basis, the number, composition, and concentration 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)

4.2 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.

NAACA will help implement an annual survey of all specialty gas vendors providing gaseous standards to the monitoring organizations and identify the monitoring organizations willing to participate in the AA-PVGP. The representative will help select the cylinders and participants in the program, assist on technical questions/issues, and provide overall consultation on the program that can be communicated back to the NACCA community.

4.3 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 advertising for participation in the program among the tribal monitoring community, and plays the same role as the NACAA representative.

4.4 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 final measurement results to monitoring organization participants, other government entities, producers, the regulated community, other interested parties, and the general public.

As addressed in the AA-PGVP Implementation Plan[1], OAQPS will provide the majority of funding resources associated with the program. Funding will relate to necessary equipment, repairs, consumable/supplies and shipping.

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

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

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. It will not assign number to distributors or distribution points of a protocol gas. 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 an EPA 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 their results as either being greater than 2% or less than 2%. 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 first to the participating monitoring organizations and then posting them on an EPA website that is accessible to the public. 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 Air Quality System (AQS) can accept this information.

OAQPS is responsible for preparing a quality assurance project plan (QAPP) for the AA-PGVP. The QAPP will conform to *EPA Requirements for Quality Assurance Project Plans* (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.

4.5 Region 2 and 7 Regional Analytical Verification Laboratories (RAVLs)

The RAVLs 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.

The monitoring organizations gaseous standards must be delivered to the RAVL 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 (see Section 12) 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 RAVLs are responsible for contributing to this AA-PGVP QAPP. The RAVLs will assist by contributing to sections involving the 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 *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards* (EPA, 1997).

Each 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 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 RAVLs are 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 NIST traceable reference material (NTRM) or SRM numbers used in the analysis against the NIST inventory of these standards. If a gas manufacturer’s internal standard (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 RAVLs will prepare draft verification results (see Section 6.2) for OAQPS and monitoring organization review.

The RAVLs may consult with those producers whose EPA Protocol Gases have differences that exceed the ± 2.0 percent accuracy acceptance criterion of 40 CFR Part 75. Upon receipt of the results of the producers' reanalysis, the RAVL will report the reanalyzed concentrations, along with the original RAVL results, to EPA in its final verification results. It is responsible for sending the certificates and its inspection results with the final verification results to OAQPS.

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

4.6 Monitoring Organizations

The monitoring organizations that are conducting monitoring under 40 CFR Part 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, if one exists. If not OAQPS will assign unique identification number.

Monitoring organizations will work with EPA to identify the universe of specialty gas producers providing protocol gases. This will entail providing information on a survey (see Appendix A). The survey will also be used for monitoring organizations to indicate whether it plans to purchase protocol gas in the upcoming calendar year, when it plans to purchase the cylinder, and whether it would like to be an active participant in the program (shipping cylinders for verification).

It is anticipated that the RAVLs will set up a quarterly analysis schedule. The participating monitoring organizations will be placed on a list that includes the approximate timeframe they have indicated a cylinder purchase and will be grouped within the appropriate analysis quarter. The AA-PGVP will keep in contact with the monitoring organizations in order to ensure the cylinder purchase is on track and that the cylinder will be available for the quarterly analysis. Therefore, the monitoring organizations must work within the quarterly schedule and in general be able to have the protocol gas cylinder remain 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 its certificate of analysis. They must have at least 6 months left in its certification period.

In order to ship cylinders to EPA, monitoring organizations will need to be trained/certified for shipping 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. For those who do not but would like to participate in the AA-PGVP, EPA will be funding on-line or web based training seminars that will provide certification for those monitoring organization.

Monitoring organizations will receive results of verifications within 3 weeks of the analysis. Unless the data are qualified for some reason, the results will be considered valid, having gone through internal quality control, verification and validation activities. If results are higher than expected, 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.

4.7 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 *EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards* from time to time to reflect technological advances in gas metrology and statistics. Throughout this QAPP, the document will be referred to as the *Protocol Gas Document*. The protocol allows producers of gaseous standards, users of gaseous standards, and other analytical laboratories to establish traceability between their protocol gases and gaseous Standard Reference Materials (SRMs) produced by the National Institute of Standards and Technology (NIST). Parts 50, 58, 60, and 75 of Title 40 of the *Code of Federal Regulations* (CFR) require using SRMs or gaseous standards traceable to SRMs for calibrating and auditing ambient air and stationary source pollutant monitoring systems. ORD has the responsibility for publishing the revised protocol and posting it on an appropriate EPA website that is accessible to the public.

As resources permit, OAQPS will invite APPCD to lead technical systems audits of this program as described in Section 20.

4.8 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 as defined in Section 2.1.4 of the *Protocol Gas Document*. 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 they feel are acceptable 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.

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. If resources permit, EPA will try to accommodate these requests by setting up a specific timeframe when these verifications can be implemented. This timeframe will be announced on AMTIC[2].

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

5.0 Problem Definition/Background

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. 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[1]). 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 or NIST standards as their calibration gases.

The original protocol never specified that EPA Protocol Gases would have any given uncertainty and it did not establish acceptance criteria for the uncertainty. In 1997, EPA revised the protocol to establish detailed statistical procedures for estimating the total uncertainty of these gases (EPA, 1997). The acceptance criterion that is required for EPA's Acid Rain Program (EPA, 1993) is for the total uncertainty to be less than +/- 2.0 percent relative.

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. The intent of these audits was to:

- increase the acceptance and use of EPA Protocol Gases as calibration gasses
- provide a quality assurance (QA) check for the producers of these gases; and
- assist users to 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.

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1 Decker, C.E., M.L. Saeger, W.C. Eaton, and D.J. von Lehmden. 1981. "Analysis of Commercial Cylinder Gases of Nitric Oxide, Sulfur Dioxide, and Carbon Monoxide at Source Concentrations." *Continuous Emission Monitoring—Design, Operation and Experience*, APCA Publication No. SP-43, Air Pollution Control Association, pp. 197-209.

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 (http://www.epa.gov/ttn/).

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 2 and 7 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 RAVL has quantified and validated the data. 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 size of EPA Protocol Gases from any one specialty gas producer to yield a statistically rigorous assessment of the accuracy. 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 explanation on how the results should be interpreted.

6.0 Project/Task Description

The purpose of this element is to provide a background of the types of activities to be conducted, the measurements that will be taken and the associated quality assurance/quality control (QA/QC) goals, procedures, and timetables for collecting the measurements. Due to the nature of the verification activity, OAQPS has identified a Category 1 QAPP for this program.

6.1 Description of Work to be Performed

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 to provide verifications of 40 cylinders per lab or 80 cylinders total per year. Cylinders will be verified at a pre-determined time each quarter.

Yearly Selection

The Protocol Gas Advisory Group will decide the number, composition and concentration of the EPA Protocol Gases that will be verified in a given year. The selection process (based on the 80 cylinder maximum is goal) is:

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

Analysis

The RAVLs will set up a 2-3 week period each calendar quarter for cylinder verification analysis. 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.

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 7 or 2

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 *Protocol Gas Document*. This information, once validated, will be sent to OAQPS which will notify the specialty gas producers, the monitoring organization providing the cylinder, and will indirectly notify all interested parties by posting the verification results on an appropriate EPA web site(s).

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.

6.2 Quality Control Goals

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.

6.2.1 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: shipping to the RAVL, laboratory storage, the verification process, and shipping back to the monitoring organization. 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 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 it will complete the appropriate sections of the chain of custody form which will accompany the cylinder and verification results that are sent back to the monitoring organizations.

6.2.2 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, and accuracy
- Records related to the acquisition of NIST SRMs and there expiration date.
- Written procedures for calculation of measured concentrations
- Estimated total uncertainty of the measured concentrations

Section 14 will cover the QC checks in detail.

6.2.3 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 (scanned and/or copied);
- 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 including all information in the Measurement Data Workbook (MDW); 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 appendix A 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.

6.2.4 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.

Verification of Laboratory Personnel to implement Gas Standard Assays:

The EPA OAQPS QA Manager will verify personnel who are capable of performing the AA-PGVP through a technical systems audit (see Section 20) of the laboratory technician's implementation of the AA-PGVP standard operating procedures and adherence to the QAPP.

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

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. OAQPS will invite personnel from the Office of Research and Development (ORD) to perform a TSA on the RAVLs every 3 years. All results of PTs and TSAs will be posted on an EPA Website.

RAVL Comparison Tests.

Two times a year the RAVL will exchange standards with each other in order to test the RAVLs comparability in assaying the same cylinder. It is expected that the labs relative percent difference of its measured concentration will be < 2%.

6.3 Timeline

The following provide the necessary time line sequence for a yearly cycle in the AA-PGVP.

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 (for previous years results)

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 Feb 1) 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) are required. These modifications will be made as soon as needed but documented, at a minimum, before the start of the next calendar year.

7.0 Data Quality Objectives and Criteria for Measurement

The purpose of this element is to document the DQOs of the project and to establish performance criteria for the environmental data operation (EDO) that will be used in generating the data.

7.1 Data Quality Objectives

DQOs are qualitative and quantitative statements derived from the DQO process that clarify the monitoring objectives, define the appropriate type of data, and specify the tolerable levels of decision errors for the monitoring program. By applying the DQO process to the development of a quality system for AA-PGVP, EPA guards against committing resources to data collection efforts that do not support a defensible decision.

As indicated in 40 CFR Part 75 Appendix A, EPA Protocol Gases must have a certified uncertainty (95 percent confidence interval) that must not be greater than plus or minus (±) 2.0 percent of the certified concentration (tag value) of the gas mixture. This acceptance criteria is for the Acid Rain Program. The AA-PGVP will adopt it as its data quality objective and develop a quality system that will allow the RAVLs to determine whether or not and individual protocol gas standard concentration is within ± 2% of the certified value. The Ambient Air Program has never identified an acceptance criteria for the protocol gasses. Since the AA-PGVP has not been established to provide a statistically rigorous assessment of any specialty gas producer, the RAVLs will report all valid results as analyzed. Monitoring organizations will take whatever actions it deems necessary upon receipt of results but it is suggested that any difference greater than 4-5% would be cause for concern.

Proposed Measurement Quality Objectives for Precision and Bias Data Quality Indicators

Based upon the criteria above, the quality of the data must be evaluated and controlled to ensure that it is maintained within the established acceptance criteria. Measurement quality objectives (MQOs) are designed to evaluate and control various phases (e.g., sampling, preparation, analysis) of the measurement process to ensure that total measurement uncertainty is within the range recommended by the DQOs. The MQOs can be defined in terms of the following data quality indicators:

Precision—A measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error.

Bias—The systematic or persistent distortion of a measurement process, which causes error in one direction. Bias will be determined by estimating the positive and negative deviations from the true value as a percentage of the true value.

Representativeness—A measure of the degree in which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Detectability—The determination of the low-range critical value of a characteristic that a method-specific procedure can reliably discern.

Completeness—A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions.

Comparability—A measure of confidence with which one dataset can be compared to another. By the RAVL use of the same SOP/QAPP, the use of NIST SRMs, and the semi - annual lab comparability check, the AA-PGVP are able to ensure the comparability of data within the lab and between the RAVLs.

"Accuracy" is a term that is frequently used to represent closeness to "truth" and includes a combination of precision and bias error components. The term "accuracy" has been used throughout the CFR and in some of the elements of this document. The AA-PGVP attempts to apportion measurement uncertainties into precision and bias components.

The AA-PGVP is a comparison based upon the concentration value derived from the R2 or R7 analyzers against the certified value of the standard. The following data quality indicators are not as important to this program:

Detectabilty- since the program will work with standards well above the instrument detection limits. Detection limit information is included on the measurement data worksheet (MDW)

Representativeness- since the program will not be able to sample enough standards from any specialty gas producer, the program will not attempt to adequately represent a producer. However aggregating the data across all producers may provide some meaningful information about the variability of standards used by ambient air monitoring organizations.

7.2 Measurement Quality Objectives

Measurement quality objectives are acceptance criteria used at various phases of a data collection system to help achieve the DQOs. Since there is no field component to this program, measurement quality objectives will focus on those laboratory activities that will ensure that the verifications are made using standards and instrumentation that are within the acceptance criteria indicated in Table 7-1. In theory, if these MQOs are met, measurement uncertainty should be controlled to the levels required by the DQO. The RAVL SOPs provide detailed procedures for the measurements of the majority of the requirements described in Table 7-1.

Table 7-1 Measurement Quality Objectives for the AA-PGVP

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

[1] The precision test does not need to accomplished if analyzer calibrated on same day as analysis

8.0 Special Training Requirements/Certification

For this project, no special training requirements or certifications are required. Region 2 and 7 staff have been routinely conducting standard comparisons based on the G-2 methodology described in the *Protocol Gas Document* and as written in the SOPs provided in this document. Prior to the start of the program, a TSA will be conducted by ORD APPCD and the OAQPS QA Manager. Successful implementation of the QAPP/SOPs as indicated by the TSA will certify the RAVLs qualification to implement the AA-PGVP

If either Region decides to employ new staff and/or contractors to perform the analysis, they will be thoroughly trained in the SOPs. Regional staff will audit the people performing laboratory analysis and certify through the audit documentation that they are qualified to perform the analytical techniques and QA required for this program. Audit documentation will be filed as described in Section 9

In order to ship cylinders to EPA, monitoring organizations will need to be trained and certified for shipping 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. For those who do not but would like to participate in the AA-PGVP, EPA will be funding on-line or web based training seminars that will provide certification for those monitoring organization. OAQPS will keep records of monitoring organization receiving this certification.

9.0 Documentation and Records

The purpose of this element is to define the records critical to the project, the information to be included in reports, the data reporting format, and the document control procedures to be used.

A document, from a records management perspective, is a volume that contains information, which describes, defines, specifies, reports, certifies, or provides data or results pertaining to environmental programs. As defined in the *Federal Records Act of 1950 and the Paperwork Reduction Act of 1995* (now 44 U.S.C. 3101-3107), records are: "...books, papers, maps, photographs, machine readable materials, or other documentary materials, regardless of physical form or characteristics, made or received by an agency of the U.S. Government under Federal Law or in connection with the transaction of public business and preserved or appropriate for preservation by that agency or its legitimate successor as evidence of the organization, functions, policies, decisions, procedures, operations, or other activities of the Government or because of the informational value of data in them..."

The following information describes the document and records procedures for the AA-PGVP. In EPA's QAPP regulation and guidance, EPA uses the term "reporting package," which will be defined as all of the information required to support the concentration data reported to EPA. This information includes all data required to be collected, as well as data deemed important by the AA-PGVP.

9.1 Documents and Records for AA-PGVP

Section 19 lists the raw data that will be collected, saved and archived for the PGVP. Table 9-1 provides the documents and records that will be kept for the program**.**

9.1.1 File Format

All information for the AA-PGVP for a particular year will be filed using the following file naming convention.

1. Program Identifier: AAPGVP
2. Region : R2 or R7
3. Year: YYYY

The AA_PGVP files will be further separated by quarter (Q1 – Q4) for:

- COC forms
- measurement data workbook
- cylinder specific correspondence.
- verification reports

Table 9-1 AA-PGVP File Structure

Program Identifier	AA-PGVP	
Region		
Year		
PGVP File Code Function	Category	Record/Document Types
PM	**Program Management Files**	• AA-PGVP Implementation Plan • Participant Surveys
CO	**Communications Files**	Telephone record and e-mail communication between • RAVL and Monitoring Orgs • RAVL and OAQPS • Other
QA	**Quality Assurance Files**	• AA-PGVP QAPP • TSAs • Instrument and Standard Certifications • QA/QC Reports • ADQs • Data validation summaries • Assessment Findings • Assessement Finding Response Forms
TE	**Technical Files**	• Standard operating procedures (SOPs) • COCs (by Quarter) • Documentation of instrument inspection and maintenance • Laboratory notebook • Calibration Records • Procurement logs • Inventories of capital equipment, operating supplies, and consumables • Repair and maintenance (e.g., vendor service records, calibration records)
DF	**Data Files**	• MDWs (by Quarter)
RE	**Reports**	• Data/summary/monthly field activity reports • Verification Reports (by Quarter) • Journal articles/papers/presentations
TR	**Training**	• Training audit document • Training materials

9.1.2 Notebooks

Laboratory notebooks- will be uniquely numbered and be associated with each AA-PGVP instrument. The notebook will be used to record calibration dates, analytical runs, routine maintenance information and any information that may support a particular analytical run.

Field/Laboratory Binders- Three-ring binders, which will be issued to each RAVL, and will contain the Chain of Custody Forms as well as inspection and maintenance forms and SOPs.

9.1.3 Electronic Data Collection

All raw data required for calculating concentrations, including QA/QC data, are collected electronically through the measurement data workbook (MDW) or on the data forms that are included in the Laboratory SOP. Laboratory data will be collected electronically and transferred to excel spreadsheets that will be used to electronically calculate a final concentration, quality control information and provide the data comparison against the certified value. More details about this process can be found in Element 18.0, *Data Acquisition Requirements*, and Element 19.0, *Data Management*.

Various hard copies are created from electronic systems, such as reports and spreadsheets used by the RAVL and others. Hard copies that are determined to be permanent record (e.g., data that lead to significant findings or conclusions) will be filed as a data reporting package to ensure that all AA-PGVP data are properly archived.

9.1.4 Hand-Entered Data

There will be some data forms that will be entered by hand. These can be found at the end of the RAVL SOPs. All hard copy information will be completed in indelible ink. Corrections will be made by inserting one line through the incorrect entry, initialing this correction, and placing the correct entry alongside the incorrect entry, if this can be accomplished legibly, or by providing the information on a new line.

9.1.5 E-mail and Attachments

OAQPS and RAVL will create file folders for AA-PGVP Correspondence. Personnel participating in the program will save any emails that they consider important to the project either in relation to changes/revisions to the Implementation Plan/QAPP/SOPs, changes to analysis timelines and correspondence among monitoring organizations and producer participants.

9.2 Data Reporting Package Archiving and Retrieval

The information discussed above will be retained for 4 years, and it is based on a calendar year (i.e., all data from calendar year 2009 will be archived until 12/31/2013). Upon reaching the 4-year archival date, hardcopies records can be disposed of. Electronic data will be maintained in archive indefinitely.

10.0 Sampling Design

The purpose of this element is to describe all of the relevant components of the AA-PGVP sampling design, the key parameters to be estimated, the number and types of samples to be expected, and how the samples are to be collected. In order to provide efficiencies and avoid redundancies:

- Section 5 described the background of the program and identified the requirement in 40 CFR Part 58 Appendix A, and

- Section 6.0 details the critical time lines and activities for the AA-PGVP.

10.1 Rationale for the Design

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 to provide verifications of 40 cylinders/lab or 80 cylinders total/year. Cylinders will be verified at a pre-determined time each quarter. The selection goal in the following order would be:

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

The design is a function of available resources. This program is considered a verification program because its current implementation level does not allow for a large enough sample of EPA Protocol Gases from any one producer to provide a statistically rigorous assessment of a producers accuracy. 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 explanation on how the results should be interpreted.

The intent of the sampling design is to determine with reasonable certainty, that a standard is within $\pm$ 2% of its certified value and the measurement data bias is within the MQOs described in Section 7.0. The sampling design will allow:

- each producer supplying protocol gasses to ambient air monitoring organizations to have one cylinder verified.

- a blind selection of gaseous standards. Since the standard will be purchased by and shipped to the monitoring organization, the producer will not be aware (or should not be made aware) of the cylinder chosen for verification from the producers inventory.

Data quality assessments will be aggregated at the following levels:
-

- **Producer-** Standards from one manufacturer
- **Pollutant-** Different pollutants may/may not have different amounts of variability
- **Concentration-** Concentrations of standards may/may not have different amounts of variability

For this program, due to the potential for small sample sizes for any producer, the most important evaluation will be at the individual cylinder and therefore the program will attempt to ensure that the results for individual comparisons are reliable.

10.2 Design Assumptions

The assumptions that are made for this verification include:

- The gas standards sent to the RAVL meet the requirements specified in the protocol gas document.

- The gas shipped to the RAVL is “blind” in that it is considered a “typical” protocol gas that has been sent by a producer and the producer does not know it will be used in the AA-PGVP.

- The protocol gas standard has not been tampered with.

10.3 Procedure for Locating and Selecting Environmental Samples

As described in the AA-PGVP Implementation Plan, each year (around Nov. of the previous calendar year) OAQPS, with the assistance of the TAMS Center and NAACA, will conduct a survey of every PQAO reporting ambient air data to AQS. The survey provides information on what specialty gas producers the monitoring organizations are using, whether they plan on purchasing standards for the upcoming calendar year and whether they would be willing to participate in the PGVP. The information collected from this survey will be used to identify the approximately 80 gaseous standards to be compared in the calendar year.

11.0 Sampling Methods Requirements

The AA-PGVP will use the participant survey to identify what specialty gas producers are being used. EPA will also identify gas production facilities and if possible, will select a cylinder from each producer's production facility (as long as all producers are initially chosen). Selection of a monitoring organization participant for each producer will be chosen at random. If monitoring organizations use a specialty gas producer but do not wish to participate in the program, EPA may be required to work directly with the producer to acquire a cylinder. If this occurs, the cylinder will be appropriately labeled and flagged identifying it status as “non-blind”

Gaseous standards are ordered by the monitoring organization as a routine aspect of ambient air monitoring. If a monitoring organization is participating in the AA-PGVP they will receive a cylinder from the specialty gas producer, avoid tampering with it and maintain it in a secure location until shipping to the RAVL.

12.0 Sample Handling and Custody

To ensure the validity of the verification, the standard gases must be delivered to the RAVL in the same condition as when they were delivered to the monitoring organization. Any use of or tampering with the gases prior to its measurement would render the verification results as questionable. Cylinders must be handled in such a manner that its integrity is beyond question. Handling includes: shipping to the RAVL, laboratory storage, the verification process, and shipping back to the monitoring organization.

At the Monitoring Organization--

Upon delivery to the monitoring organization, the gas cylinders will not be used nor tested for any reason prior to shipping to the RAVL. The cylinder valve should remain shrink wrapped. Cylinders are delivered with a certificate which includes a cylinder pressure. The pressure will be tested upon arrival at the RAVL to ensure changes to the cylinder pressure have not occurred. The gas standards will be placed in a secure location and prepared for transport to the RAVL.

Each quarter the RAVL will have scheduled a specific week for the verification. Monitoring organizations, based upon there purchases of cylinders, will have been given a specific quarter and timeframe on when to ship their standards to the RAVL. The monitoring organization will be provided with a chain of custody (COC) form which they will initiate. The chain of custody is found in Appendix B. The COC form will be emailed to the RAVL the day of shipment and a hardcopy will also be shipped with the cylinder.

At the RAVL--

Upon receipt of the standards at the RAVL, the lab will complete the receipt-portion of the COC. During receipt, the RAVL will confirm the certified cylinder pressure. This will, at a minimum, confirm that no tampering has occurred. .

EPA laboratory facilities are secured environments. Identification is required to get into the facilities as well as into the various laboratory buildings. Once the gas standards have been logged in at receiving, the RAVL will store cylinders in a secure laboratory location with limited access and by all EPA laboratory safety standards. The shrink wrap will remain on the cylinder valve until testing begins.

Upon completion of the verification, the RAVL will complete the final portion of the COC and email a copy to the monitoring organization. The RAVL will also include a hardcopy of the COC form with the standard when shipping the cylinder back to the monitoring organization. The lab will include the final cylinder pressure (after verification) so that the monitoring organization can determine whether any tampering or loss of gas occurred during shipping.

13.0 Analytical Methods Requirements

The RAVL will follow the procedure G2: *Assay and Certification of a Compressed Gas Calibration Standard Using Dilution* as described in the *Protocol Gas Document*. Figure 13.1 provides a simple schematic. The procedure is similar to Figure 2-4 in the *Protocol Gas Document* with the exception that a zero air generator instead of a zero gas cylinder is used.

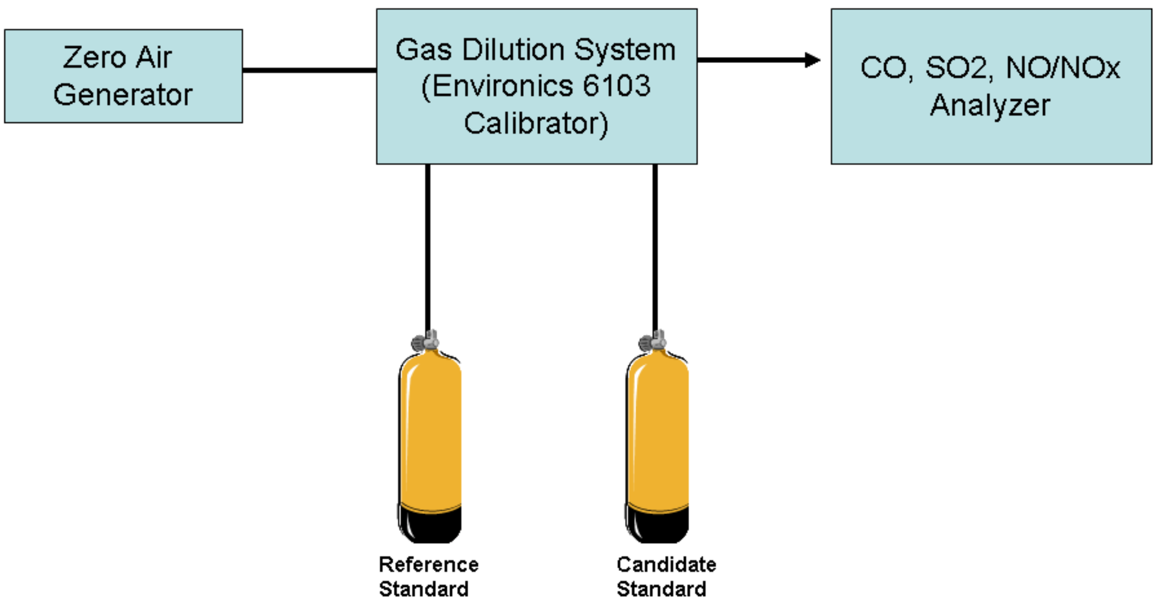

Figure 13.1 AA-PGVP Verification G2 procedure

This procedure is used to assay the concentration of a diluted candidate compressed gas calibration standard, based on the concentration of a diluted compressed gas reference standard of the same gas mixture. The procedure will be used to verify CO, SO2, NO and NOx in specialty gas producer calibration standards. This procedure allows the RAVL to certify that the assayed concentration for the candidate standard is traceable to the reference standard. The procedure employs a low-concentration-range (i.e., ambient air quality level) pollutant gas analyzer to compare quantitatively diluted gas samples of both the candidate and reference standards. The procedure may be used for the assay of multiple candidate standards at the same time. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards.

The Region 2 and 7 RAVL have worked together to develop similar standard operating procedures (SOP) for this program thereby ensuring laboratory and data comparability. The RAVL SOPs are an adaptation of the G2 procedure discussed above but will reflect specific details related to the RAVL laboratories, the types of equipment, standard reference materials used and the specific QA/QC employed.

A mass controlled gas calibrator will be used to dilute NIST Standard Reference Materials (SRM) to monitoring organization protocol gas. The resulting diluted gas will be analyzed using an EPA reference or equivalent analyzer. Flow calibrations will be based on a primary flow standard (BIOS ML-800 or BIOS Definer 220). The SOPs for this program can be found in Appendix C.

The SOP will be followed as written unless:

- Changes in G2 require changes in the SOP
- TSAs uncover findings that need correction to the method.
- New instrumentation requires a change.

If a change is needed to improve data quality, it will be instituted immediately and a record, in the form of a quality bulletin (see Fig. 13.2), will document the reason for the change, and the affect it had on samples prior to the change. An addendum will be made to the SOP that will cover the change until there is time for the SOP to be revised. Changes that do not effect the quality of data but are either grammatical in nature or provide an alternate acceptable procedure will be made on an annual basis prior to the start of the calendar year.

Quality Bulletin

Subject:

Number ____________________
Date ________________________
Page __________of __________
Supersedes No. ______________
Dated ______________________

Replace and Discard Original

Add Material to Document

Notes:

____
AA-PGVP QA Coordinator

Retain this bulletin until further notice ☐
Discard this bulletin after noting contents ☐
This bulletin will be invalid after (Date) ______________ ☐
This bulletin will be incorporated into quality ☐
Procedure No. _____________ by (Date) ______________ ☐

Figure 13.2. Quality bulletin

14.0 Quality Control Requirements

To assure the quality of data from air monitoring measurements, two distinct and important interrelated functions must be performed. One function is the control of the measurement process through broad QA activities, such as establishing policies and procedures, developing DQOs, assigning roles and responsibilities, conducting oversight and reviews, and implementing corrective actions. The other function is the control of the measurement process through the implementation of specific QC procedures, such as audits, calibrations, checks, replicates, and routine self-assessments. In general, the greater the control of a given monitoring system, the better will be the resulting quality of the monitoring data.

QC is the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that the stated requirements established by the customer are met. In the case of the Ambient Air Quality Monitoring Network, QC activities are used to ensure that measurement uncertainty, as discussed in Section 7, is maintained within acceptance criteria for the attainment of the DQO.

All the statistical calculations for all the required QC, as described in Appendices A and C of the *Protocol Gas Document* are followed for this program and are included in the Measurement Data Workbook that is included in the RAVL SOPs in Appendix C.

14.1 QC Procedures

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.

14.1.1 Cylinder Integrity

As mentioned in Section 6 and 12, to ensure the validity of the verification, the monitoring organizations gas standards 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. 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 Appendix B. 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 it 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.

14.1.2 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 and the MDW
- Written procedures for calculation of measured concentrations
- Estimated total uncertainty of the measured concentrations

Table 7-1 in Section 7 provides the QC checks that will be implemented for this program.

All checks, data reduction techniques and statistical equations used for the checks will follow the criteria and worksheets described in Section 2 (G2) of the *Protocol Gas Document.* Summary information is included in this section.

Calibration--

Calibrations of the mass flow controller and the ambient air analyzers are discussed in 16.0

Day of Audit Zero and Span Verifications

On any analysis day, following the multipoint calibration, zero and span gas checks must be conducted prior to any assay of standards. The exact zero and span check procedures for the respective NO, SO2, and CO analyzers can be found in *EPA Region 2 Standard Operating Procedures for Calibrating Ambient Air Analyzers for G2 Gas Assays.* At least 3 discrete zero point and span points will be measured and two estimates of the zero and span verifications will be made: 1) the standard error of the mean, and 2) the relative difference

The standard error of the mean is calculated as

$$\frac{s}{\sqrt{n}} \leq \frac{\overline{R_{DRS}}}{100}$$

Where:

s = standard deviation of the analyzer's response;
n = the number of independent measurements of the gas mixture; and
$\overline{R}_{DRS}$ = the mean analyzer response to the diluted reference standard.

The standard error of the mean for each set of measurements must be less than or equal to 1.0 percent of the mean response to the diluted reference standard.

The relative difference (RD) is calculated as

$$100\left[\frac{\text{Current Response} - \text{Calibration Response}}{\text{Calibration Response for Diluted Standard}}\right]$$

Where the

current response = either the mean zero response or the mean reference standard response
calibration response = the diluted reference standard, even when zero gas is being measured

If the relative differences for the zero and span checks are less than or equal to 5.0 percent, the analyzer is considered to be in calibration

Precision Test

Using the highest concentration standard SRM to be used that day, the pollutant mass flow controller will be set to 70 cc/min, and the appropriate zero gas dilution will be selected to give a span concentration >80% of the analyzer URL. Three discrete measurements of analyzer response will be made at this concentration, alternated with 3 zero gas measurements. The precision criterion for these measurements is a standard error of the mean <1.0% of the mean response of the diluted standard (see the EPA Protocol section 2.3.5.4)

Routine Data Check

To ensure the accuracy of the assay, any standard that is greater than 2% of the certified value will be run 3 times to ensure an accurate assay. If the majority of the day's assays are within the acceptance range and any one of the additional assays for a cylinder in question comes within the acceptance limit, the acceptable value will be used. The RAVL will not go beyond 3 checks of a cylinder.

Lab Comparability Check

Twice a year the RAVL will exchange a cylinder that both RAVL labs will characterize. The cylinder can be one from the monitoring organization, a routine protocol gas cylinder used for calibration in the lab or an SRM. The objective is to establish that the laboratory activities and analysis provide comparable results. The standard will be characterized three times by each laboratory and the mean value will be used for comparison. The relative percent difference (RPD) of the measurements will be calculated as:

$$RPD = \frac{Lab1 - Lab2}{(Lab1 + lab2)/2} \bullet 100$$

The RPD acceptance is $\pm$ 2%.

15.0 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The purpose of this element is to discuss the procedures used to verify that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels. All instrument inspection and maintenance activities are documented and filed.

15.1 Testing

15.1.1 Equipment Testing

The following equipment is used in the PGVP

- Thermo 48C and 48i CO analyzers
- Thermo 43i SO2 analyzer
- Thermo 42i NO/NOx analyzer
- Environics 6103 gas phase titration calibrator
- Primary flow standard (BIOS ML-800 and BIOS Definer 220)

Instruments used for the AA-PGVP have been used for similar verifications by Regions 2 and 7 and are known to be suitable for this activity. Testing of this equipment occurs through the use of NIST Standard Reference Materials (SRMs). The SRMs are used to calibrate the equipment, perform ongoing QC checks and are used as the known concentrations from which the verification is performed.

Failure of the analyzers, based upon QC checks, will result in troubleshooting and re-calibrations. If trouble shooting and recalibration is not successful, Thermo will be notified. Thermo has thoroughly checked all instruments in 2010 and the R2 RAVL has set up a service agreement with Thermo that will guarantee repair in three days or a replacement will be provided until repair and successful operation of original.

15.1.2 SRM Testing

The following SRMs will be purchased by the RAVLs:

- NIST SRM 2639a CO @ 10,000 ppm
- NIST SRM 2638a CO @ 5,000 ppm
- NIST SRM 1694a SO2 @ 100 ppm
- NIST SRM 1693a SO2 @ 50 ppm
- NIST SRM 1684a NO @ 100 ppm
- NIST SRM 1683b NO @ 50 ppm

Since more than one SRM will be used during the verification process these “multiple verifications” will provide a check to ensure that a particular SRM is not contaminated. As new SRMs are purchased, they will be checked against the older cylinders to ensure cylinder integrity.

Since the concentration of the SRMs are key to a successful PGVP, their expiration date will be monitored and will be re-verified by NIST before the expiration date. This reverification, with an acceptable result, will provide assurance of the quality of the verification data.

15.2 Inspection

Inspection of various equipment and components can be subdivided into the laboratory and field activities.

15.2.1 Inspection in the Field

The only item to inspect in the field is the gas standard that the monitoring organization receives from the specialty gas producer. Typically the cylinder valves will be shrink wrapped and the gas will be accompanied by a certificate of analysis (per Section 2.1.4 of the *Protocol Gas Document*) that will include the cylinder pressure. Monitoring organizations will perform an inspection to ensure that the cylinder integrity appears intact and that the certificate of analysis is complete.

15.2.2 Inspection of Laboratory Items

In addition to the analyzers, there are several items that need routine inspection in the laboratory. During every quarterly verification the following items will be inspected:

- Leaks in stainless steel CGA 660 regulators for SO2/NOx analysis
- Leaks in brass CGA 350 regulators for CO analysis
- Minimum of >20 psi zero air gas supply sufficient for 20 L/minute Environics 6103’s
- Leaks/cracks in 1/8”and ¼” o.d. thick walled Teflon tubing
- Envidas computer data acquisition system
- Leaks around ¼” and 1/8” Swagelok nuts and ferrules

15.3 Maintenance

There are items in the laboratory that need maintenance attention in the AA-PGVP. There are no maintenance activities associated with the field.

15.3.1 Laboratory Maintenance Items

The successful execution of a preventive maintenance program for the RAVL will go a long way towards the success of the AA-PGVP. Table 15-1 provides information on laboratory preventive maintenance. The laboratory notebook will document maintenance activities.

Table 15-1 Preventive Maintenance in PGVP- Laboratories

Item	Responsibility	Frequency
General laboratory maintenance/cleaning		
Table cleaning	Laboratory Analyst (LA)	Every day
Overall laboratory	LA	Once a month
Analytical Equipment		
Cleaning	LA	Every 6 months
Calibration/verification	LA	Once every 3 months
Tubing replacement	LA	as needed
Regulator cleaning	LA/Support staff	Yearly
Laboratory Computers		
Computer backup	LA	Flashdrive backup with every verification run
AA-PGVP database distribution to OAQPS	LA	Quarterly
Computer system preventive maintenance (clean out old files, compress hard drive, inspect)	PC support personnel	Yearly

16.0 Instrument Calibration and Frequency

This element of the AA-PGVP QAPP concerns the calibration procedures that will be used for instruments involved in the environmental measurements. All calibration activities are described in more detail in the RAVL SOPs (Appendix C). In addition, all calibration calculations as well as the calculations for all the required QC, as described in Appendices A and C of the *Protocol Gas Document* are followed for this program and are included in the Measurement Data Workbook that is included in Appendix C.

16.1 Laboratory Instrumentation Requiring Calibration

The equipment requiring calibration are the Environics 6103 calibrator, and the Thermo analyzers identified in Section 15.

16.1.1 Quarterly Flow Calibration of Environics 6103 calibrators

Environics 6103 calibrators, used for dilution of zero and reference/candidate standards, will have their mass flow controllers calibrated quarterly, utilizing a NIST traceable primary flow standard. In summary, the zero mass flow controller will be calibrated at flow rate settings of 16,000, 8000, and 4000 liters/minute. The pollutant mass flow controller will be calibrated at flow rate settings of 78, 70, 60, 50, and 40 cc/min. These flow rates were chosen because they cover the top 50 to 90% of the analyzers range, which is the most accurate and well characterized portion of the analyzer's response.

16.1.2 Quarterly Calibrator Dilution Check

The quarterly calibrator dilution check procedure is specified in the RAVL SOPs (Appendix C). The dilution check consists of: 1) Multipoint calibration of the ambient air utilizing a CO SRM, followed by 2) generation of 3 discrete points >80% of the instrument URL with the same calibrator using a second NIST CO SRM with a different. The acceptance criteria for the predicted response versus the analyzer response is a relative difference of <1%.

16.1.3 Quarterly Calibration of Ambient Air Analyzers

Analyzers will be calibrated quarterly within 2 weeks of the expected verification. The exact calibration procedures for the respective NO, SO2, and CO analyzers can be found in the RAVL SOPs. In summary, the ambient air analyzers will be calibrated at 5 points from 50% to 90% of the analyzer URL, plus a zero point. A 100 ppm NIST SRM for SO2 and NOX and either a 10,000 or 5,000 ppm for CO will be used. Table 16-1 provides an example the calibrator settings and the predicted concentrations

Table 16-1 Typical Example of Ambient Analyzer Calibration Settings and Predicted Concentrations

Gas Type	SRM Concentration to be used (in ppm)	The pollutant mass flow controller is set to: (in cc/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
NO/NOx or SO2	100	16000	78	0.485
	100	16000	70	0.436
	100	16000	60	0.374
	100	16000	50	0.312
	100	16000	40	0.249
	100	16000	0	0.000
CO	10000	16000	78	48.513
	10000	16000	70	43.559
	10000	16000	60	37.360
	10000	16000	50	31.153
	10000	16000	40	24.938
	10000	16000	0	0.000

17.0 Inspection/Acceptance for Supplies and Consumables

Since the AA-PGVP is a small program implemented by two regional laboratories, 2-4 laboratory analysts using supplies and consumables for about 4-8 analytical runs a year, formal procedures for the inspection and acceptance of supplies and consumables are not needed. At the beginning of each year, the RAVL will ensure that they have an adequate inventory of SRMs and consumable supplies for the verification runs expected and will inform OAQPS of its needs. OAQPS has secured funding for any purchase of supplies and consumables necessary to implement the program.

18.0 Data Acquisition Requirements

This element addresses data not obtained by direct measurement from the AA-PGVP. The majority of data used in the AA-PGVP will be direct measurements acquired by the RAVL laboratory analysts.

18.1 Acquisition of Non-Direct Measurement Data

The AA-PGVP relies on data that are generated through laboratory operations; however, some data are obtained from sources outside the AA-PGVP. This element lists these data and addresses quality issues related to the AA-PGVP.

18.1.1 Chemical and Physical Properties Data

Physical and chemical properties data and conversion constants are often required in the processing of raw data into reporting units. This type of information, which has not already been specified in the monitoring regulations, will be obtained from nationally and internationally recognized sources. Other data sources may be used with approval from the National AA-PGVP Project Leader. The following sources may be used in the AA-PGVP without prior approval:

- NIST
- International Organization for Standardization (ISO), International Union of Pure and Applied Chemistry (IUPAC), American National Standards Institute (ANSI), and other widely recognized national and international standards organizations
- The U.S. Environmental Protection Agency (EPA). Particularly relevant is the *Protocol Gas Document*
- The current edition of certain standard handbooks may be used without prior approval from the National AA-PGVP Project Leader. Two that are relevant are CRC Press' *Handbook of Chemistry and Physics* and *Lange's Handbook of Chemistry*.

18.1.2 External Monitoring Databases

It is the policy of the AA-PGVP that no data obtained from the Internet, computer bulletin boards, or databases from outside organizations shall be used in creating reportable data or published reports without approval from the National AA-PGVP Project Leader. Requests may be raised during the AA-PGVP Advisory Group conference calls or on an individual basis. This policy is intended to ensure the use of high-quality data in AA-PGVP publications.

19.0 Data Management

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

19.1 Information Needed for AA-PGVP

Information required to successfully implement the AA-PGVP include:

- **AQS**- List of active PQAOS with sites requiring gaseous calibration standards
- **Pre-Implementation Survey**- Appendix A
- **COC Form**- Appendix B
- **Measurement Data Workbook**- Appendix C (part of SOPs)

The data listed above is all that is needed to develop the reports and assessments for the program. For the first year of the program, the data listed above may be captured on hardcopy and electronically. After an evaluation of the first year efforts, OAQPS and the RAVL will evaluate the critical data input parameters and develop a more complete database to house all essential information.

19.2 Computer Hardware and Software

Software--

All information for the AA-PGVP will be collected using Microsoft products; either Excel or Word. The Pre-Implementation Survey, the chain of custody form and the MDW have been developed in Microsoft Excel

Hardware--

OAQPS will use a personal PC to record AA-PGVP information. Data will be stored on the EPA-LAN with access only by the employee and system administrator and on the C-drive of a the employees personal PC as a back-up. The LAN is backed-up every 24 hours.

Both RAVLs will have dedicated laboratory PCs that will be used to store chain of custody and MDW data and any other information pertaining to the AA-PGVP.

19.3 Data Recording

Pre-Implementation Survey --

OAQPS is responsible for collecting the Pre-Implementation Survey. The surveys are emailed to OAQPS who will store them on the personnal LAN site with access only by employee and system administrator and on the C-drive of a the employees personal PC

Chain of Custody--

The chain of custody form will be developed in Excel but monitoring organizations will be given the choice to enter their portion of the form into excel (while still submitting a hardcopy version with the gas standard) or providing it hardcopy. Once the chain of custody is received at the RAVL it will be checked against the electronic form (if sent by the monitoring organization) or it will be entered by the RAVL in Excel and saved. The RAVL will complete the form in Execl but sign the original hardcopy version and send it back to the monitoring organization.

Each method that generates information in the AA-PGVP will have a data form available for recording this information. Results of both the calibration and the resulting verification analysis will be recorded on the Measurement Data Workbook (MDW). The original MDW can be found in Appendix A of the *Protocol Gas Document*. The RAVL has revised the MDW to conform specifically to the needs of the AA-PGVP.

The MDW includes instructions that guide the user through the steps in its use. The worksheets in the Workbook are also color coded to simplify use. Table 19-1 provides a description of the various worksheets in the MDW.

Table 19-1 Worksheets in the MDW

Worksheet Name	Notes
Read Me #1	Describes the basic layout of this Measurement Data Worksheets
Assay Information	For entering serial #'s of calibrators cylinders, day of audit etc. Cells highlighted in green are locked because the information in these cells are obtained in other worksheets and reproduced in this sheet. There are no password protections for any locked cells in this, or any other sheets in this application. Scrolling to locked cells is permitted. To unprotect this and all worksheets here, Tools --> Protection --> Unprotect sheet.
Calibrator Flow Cal	Used for flow calibration of the gas dilution device used for assays and analyzer calibrations. User input is required only for the colored cells (blue and yellow). All other data is carried through from other worksheets. Uncolored data cells are protected. Meta data from the flow standards are imported starting from cell J48.
Analyzer Cal	Used to calibrate the ambient air analyzer under test.User input is required only for the colored cells. All other data is carried through from other worksheets. Uncolored data cells are protected
Calibrator Dilution Check	Used to verify that the calibrator is accurate at various dilutions. This approach is required by the method when diluted standards are used.
Measurement Data	This is an original sheet from the method 600/R-97/121. It is unmodified from the original with the exception of user entered data points as required. Numerous other worksheets in this spreadsheet will have data cut and pasted into this sheet. Additionally, data outputs calculated in this

Worksheet Name	Notes
Day of Assay Zero and Span	Used to verify that the analyzer has acceptable precision and accuracy for the assay. The methodology is specified in the original method. User input is required only for the colored cells; All other data is carried through. Uncolored data cells are protected
QA	Used as a screening device to display and verify that all QA information generated in this spreadsheet has been collected. Additionally, the status column contains, for each line; a logical test to determine if the parameter in question has been met, the result of the logical test, and a conditional color coded format depending on the answer. The entire sheet is protected, as no direct data input into this sheet is required.
Assay Worksheet	Used to input assay data, as well as to copy and paste data to the Measurement Data worksheet, and to paste the results from the Measurement Data Worksheet. The yellow highlighted cells are unprotected. Don't overlook cells N42..AC83 where the data is summarized by cylinder. The N42..AC83 range is used to paste data to and from the Measurement Data Worksheet. Clearing Row F and K for the challenge standards will put blank cells in the rest of the row. This was done to minimize clutter when analyzing less than 5 challenge cylinders.
Certificates	Used to print certificates of assays. The entire worksheet is protected, as no data is entered here, having all been carried through from the other worksheets.
Read Me, Curve 1 Residuals 1, Curves 2, Residuals 2, Curve 3 Residuals 3, Curves 4, Residuals 4, Chart Data	These worksheets are from the original method. They contain the original read me file, as well as some of the more advanced statistics used by the method. There are no user data to be entered in these sheets

The MDW contains the acceptance criteria explained in Section 7 (Table 7-1). Therefore the MDW can be used as a verification/validation tool. An example of an MDW can be found in Appendix C. It is anticipated that 3 or 4 cylinders can be verified each day (run) and it's therefore expected that approximately 3 MDW will be developed for each quarterly verification of 10 cylinders. In addition a minimum of 3 cylinders will be verified in each run. In order to identify the verification analysis run, the following file naming convention will be used:

1. Work sheet identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2 or R7
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 -XX

The following file label is an example of a MDW performed by Region 2 in 2010, in quarter 1 and is the first run for CO data

MDW_AAPGVP_R2_2010_1_C_01

This label (other than MDW code) will also be used to identify the program file for all the information captured (e.g COC, correspondence etc.) in each quarter.

19.4 Data Review, Verification/Validation

Section 22 will provide a discussion on the data review, verification and validation.

19.5 Data Transformation

Calculations for transforming raw data from measured units to final concentrations are relatively straightforward and are internally programmed into the MDW which will be checked and verified prior to the start of the program to ensure that they are performing the calculations appropriately. The RAVL SOP also includes the pertinent calculations and data transformations.

19.6 Data Reduction and Data Integrity

Data-reduction processes involve aggregating and summarizing results so that they can be understood and interpreted in different ways. For the AA-PGVP, since it is initially anticipated that only 80 cylinders per year will be verified, there is little data reduction anticipated. The uncertainty estimate will be calculated and reported for each gas standard verified. All three replicate values will be reported along with the average value (which is used for the final measured concentration). Data will be aggregated by pollutant and may be aggregated by cylinder concentration or other methods (i.e., producer method for certification). However, verification reports will always include individual cylinders concentrations (measured and certified value) and any aggregations will include the data reduction technique used so that any reader can replicate the aggregated results.

The integrity of AA-PGVP data reduction can be verified by independent review of the data and algorithms used. Verification of data integrity requires that AA-PGVP data be stored in a manner that permits any data modification to be detected. Detection of data changes is facilitated by the record keeping requirements of the AA-PGVP Laboratory SOPs, which require archiving of hard-copy records for important data (such as analytical batch reports, MDW and COC Forms). These archived records enable EPA to trace the raw data used in final verification reports.

In addition, AA-PGVP Laboratory SOPs require that copies of the laboratory information systems (LIMS) data are archived into read-only media (e.g., CD-ROM or back-up tape) and regularly stored at an off-site location. These archival database copies may also be used to evaluate data integrity and to check that data used in a particular verification match the data on hard-copy records.

19.7 AA-PGVP Data Transfer and Archiving

Upon completion of verification/validation and rectification of any issues, final results for each quarter of analysis will be provided to OAQPS. The RAVL will send the MDW to OAQPS.

Upon completion of a year of data, the 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 in the following calendar year) or as an update to the report. Table 19-2 presents information such as where various data are produced, and how/when it will be archived/transferred.

Table 19-2 Data Transfer and Archiving

Data Produced	How to Archive	When to Transfer
Pre-Implementation Survey	Save on OAQPS LAN and on flash drive in local file.	Upon completion of survey transfer a copy to RAVL
COC	Monitoring organization saves copy	Transfers copy with cylinder to RAVL.
AA- PGVP MDW	Save on RAVL data base and on flash drive in file. Hardcopy of MDW in file	Upon data validation transfer data via email to OAQPS quarterly
RAVL	Back-up of database occurs each night as per laboratory computer network storage procedures	Validated data to AQS once a year (if implemented.

There is a possibility that AA-PGVP will be uploaded to AQS. If this does occur, concentration data will be uploaded to the AQS database in a Precision & Accuracy Transaction. AQS will develop the programs necessary to perform the uncertainty calculations explained in the Protocol Gas Guidance Document.

19.8 Data Tracking

Data tracking will begin with the Participant Survey information. Once the participating monitoring organizations are selected, a AA-PGVP Annual Data Tracking Form will be created that will include the information listed in Table 19-3

Table 19-3 AA-PGVP Annual Data Tracking Form Information

Monitoring Organization Name	Primary Quality Assurance Organization #	Reporting Organization #	Point Of Contact
Point Of Contact email	RAVL Selected	Quarter for Verification	Cylinder # Received
Date of Cylinder Receipt at RAVL	Date of RAVL Analysis	Date of RAVL Validation	Date Shipped back to Monitoring Organization
Date Quarterly Results Delivered to OAQPS	Date Results Posted on AMTIC	Date results submitted to AQS (if implemented)	Comments

Monitoring organizations that are selected for participation will be sent an email that will provide them information on the RAVL they will be sending a cylinder to and the quarter for verification. The monitoring organizations will then send an email the day they ship gas standards to the RAVL. This information along with the COC information about the cylinder will be added to Data Tracking Form. Upon completion of verification and validation the Data Tracking Form will be updated. When the gas standard is shipped back to the monitoring organization, the Data Tracking Form will be updated and when results are sent to OAQPS for final uploading, the Tracking Form will be completed. This information will be all that is necessary to track that monitoring organizations and cylinders selected for verification where accomplished. If the record is not complete then a comment will be added to explain why a certain step in the process was not completed.

19.9 Data Storage and Retrieval

Table 19-4 shows archival policies for the AA-PGVP data.

Table 19-4. Data Archive Policies

Data Type	Medium	Location	Retention Time	Final Disposition
Participation Surveys	electronic	OAQPS	Indefinite	N/A
Chain-of-Custody Forms	Hard copy Electronic	RAVL RAVL	4 years Indefinite	Discarded, with permission from OAQPS
Laboratory notebooks	Hard copy	RAVL	4 years	N/A
AA-PGVP MDW	Electronic (online)	RAVL & OAQPS	Indefinite	Back-up media retained indefinitely
Data Tracking Form	Electronic	RAVL & OAQPS	Indefinite	N/A

The PGVP data reside on a Microsoft Windows-compatible computer in the RAVL. The security of data in the system is ensured by using the following controls:

- Network security passwords for access to the project and database files
- Regular password changes (as specified by EPA network security)
- Storage of media, including back-up tapes in locked, restricted access areas.

19.10 Information Management Security

The AA-PGVP data is maintained on an EPA file share, and access is restricted to authorized personnel. Data can only be released with the express permission of the National AA-PGVP Project Leader. Only validated, approved data are reported, where the information becomes public domain.

20.0 Assessments and Response Actions

For the purposes of this QAPP, an assessment is defined as an evaluation process used to measure the performance or effectiveness of the quality system and various measurement phases of the data operation.

The results of assessments indicate whether the QA/QC efforts are adequate or need to be improved. Both qualitative and quantitative assessments of the effectiveness of these control efforts will identify those areas most likely to impact the data quality.

To ensure the adequate performance of the quality system, the AA-PGVP will perform the following assessments:

- TSAs
- Audits of data quality (ADQs) as part of the TSA
- Data quality assessments (DQAs)
- Performance Evaluations.

20.1 Assessment Activities and Project Planning

20.1.1 Technical Systems Assessment

A TSA is an evaluation of a data collection operation or organization to establish whether the policies, practices, and procedures are adequate for ensuring that the type and quality of data needed are obtained. The TSA basically determines whether the RAVL is following both the QAPP and SOP and are therefore following procedures that would provide data of acceptable quality for achieving the PGVP's objectives.

TSAs of the RAVL will be conducted by EPAs Office of Research and Development (ORD) Air Pollution Prevention and Control Division (APPCD) every three years. APPCD is responsible for the development and revisions of the of *Protocol Gas Document*[1]. NIST and OAQPS will also be invited to attend this TSA. Results of this TSA will be posted on the AMTIC Website[2].

The TSA can be accomplished by a team or by an individual assessor. Key personnel to be interviewed during the assessment are those who have responsibilities for planning laboratory operations, QA/QC, data management, and reporting. The TSA will review the following two activities:

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[1] EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121).

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

- **Laboratory.** Sample receipt, sample preparation, analysis, archiving, QA/QC and record keeping.
- **Data management.** ADQs, Information collection, flagging, data editing, security, and upload.

The TSA team will prepare a brief written summary of findings organized into the areas described above. Problems with specific areas will be discussed, and an attempt will be made to rank them in order of their potential impact on data quality. For the more serious of these problems, the TSA team will summarize assessment findings on the Assessment Finding Form (Figure 20-1).

Assessment Finding

Assessment Title: ______________ Assessment #: _______________
Finding #: ______________

Finding:

Discussion:

QA Lead Signature: ______________________ Date: _____________

Assessed Agencies
Signature: _______________________ Date: __________________

Figure 20.1. Assessment Finding Form.

By design, an Assessment Finding Form will be completed for each major deficiency that requires formal corrective action. This form will include information such as the finding impact, estimated time period of deficiency, sample(s) affected, and reason for action. The Assessment Finding Form will notify the laboratory of serious problems that may compromise the quality of the data and therefore require specific corrective actions. These forms are initiated by the TSA team and discussed at the debriefing. If the assessed group is in agreement with the finding, the form is signed during the debriefing. If a disagreement occurs, the TSA team will record the opinions of the group assessed and set a time at some later date to address the finding at issue.

Post-Assessment Activities

The major post-assessment activity is the preparation of the assessment report. The report will include the following:

- Assessment title, number, and any other identifying information
- Assessment team leaders, assessment team participants, and assessed participants
- Background information about the project, purpose of the assessment, dates of the assessment, particular measurement phase or parameters that were assessed, and a brief description of the assessment process
- Summary and conclusions of the assessment and corrective action required
- Attachments or appendices that include all assessment evaluations and assessment finding forms.

To prepare the report, the TSA team will meet and compare observations with collected documents and results of interviews and discussions with key personnel. Expected QAPP implementation is compared with observed accomplishments and deficiencies, and the assessment findings are reviewed in detail. Within 30 calendar days of the completion of the assessment, a draft assessment report will be prepared and submitted. The TSA report will be submitted to the appropriate AA-PGVP personnel which include the RAVL lab analyst(s) and supervisor and OAQPS AA-PGVP Lead.

If the RAVL has written comments or questions about the TSA report, the TSA team will review and incorporate them as appropriate and prepare and resubmit a report in final form within 30 days of receiving the written comments. The report will include an agreed-upon schedule for corrective action implementation.

Follow-up and Corrective Action Requirements

The RAVL and OAQPS may work together to solve required corrective actions. As part of corrective action and follow-up, an Assessment Finding Response Form (Figure 20-2) will be generated by the assessed organization for each Assessment Finding Form submitted by the TSA team. The Assessment Finding Response Form will be signed by the RAVL and will be sent to TSA Lead who reviews and accepts the corrective action. The Assessment Finding Response Form will be completed by the assessed organization within 30 days of acceptance of the assessment report.

Assessment Finding Response Form

Assessed Division:____________________

Assessment Title: ____________________ **Assessment #:** _________
Finding #:________

____

Finding:

Cause of the problem:

Actions taken or planned for correction:

Responsibilities and timetable for the above actions:

Prepared by: ________________________ **Date:** _____________

Signed by: __________________________ **Date:** _____________

QA Division

Reviewed by: ________________________ **Date:** _____________

Remarks:

Is this assessment finding closed? ___________ **When?** _____________

File with official assessment records. Send copy to assessed organization.

Figure 20.2. Assessment Finding Response Form.

Other Reviews of the RAVL

On an annual basis the RAVL will setup a one week period where specialty gas producers will be able to visit and review the laboratory facilities. This available week will be advertized on AMTIC 2-3 months prior to the scheduled week.

20.1.2 Audit of Data Quality

An ADQ reveals how the data are handled, what judgments were made, and whether uncorrected mistakes were made. ADQs can often identify the means to correct systematic data reduction errors. An ADQ will be performed as part of the TSA. Thus, sufficient time and effort will be devoted to this activity so that the auditor or TSA team has a clear understanding and complete documentation of data flow. Pertinent ADQ questions will appear on the TSA check sheets to ensure that the data collected at each stage maintains its integrity. The ADQ will serve as an effective framework for organizing the extensive amount of information gathered during the audit of laboratory, field monitoring, and support functions within the agency. The ADQ will have the same reporting/corrective action requirements as the TSA**.**

20.1.3 Data Quality Assessments

A DQA is a statistical analysis of environmental data used to determine whether the quality of data is adequate to support a decision based on the DQOs. Data are appropriate if the level of uncertainty is acceptable for the decision based on the data. The DQA process is described in detail in *Guidance for the Data Quality Assessment Process* (EPA QA/G-9) and is summarized below.

- **Review the DQOs and sampling design of the program.** Review the DQOs and define statistical hypothesis, tolerance limits, and/or confidence intervals
- **Conduct preliminary data review.** Review precision and accuracy (P&A) and other available QA reports. Calculate summary statistics, plots, and graphs. Look for patterns, relationships, and anomalies
- **Select the statistical test.** Select the best test for analysis based on the preliminary review and identify underlying assumptions about the data for that test
- **Verify test assumptions.** Decide whether the underlying assumptions made by the selected test hold true for the data and the consequences
- **Perform the statistical test.** Perform test and document inferences and evaluate the performance for future use.

A DQA will be included in the *AA-PGVP Annual QA Report.* Details of these reports are discussed in Element 21.0, *Reports to Management*.

20.1.4 Performance Evaluations (non-mandatory)

Performance evaluations (PEs) are a type of audit in which the quantitative data generated in a measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst, or a laboratory[3]. NIST will be invited to audit the verification activities by challenging the measurement system with an independent set of standard reference materials. At the writing of this QAPP the implementation of this activity has not been pursued where any agreements with NIST have been reached. It is proposed that this check be accomplished annually. The semi-annual laboratory comparability check, discussed in Section 14 will serve as an internal PE.

20.2 Documentation of Assessments

Table 20-1 summarizes each of the assessments discussed above.

Table 20-1. Assessment Summary

Assessment Activity	Frequency	Personnel Responsible	Report Completion	Resolution
TSAs	1/ 3 years	ORD -APPCD , OAQPS	30 days after the activity	RAVL
ADQs	1/3 years	ORD -APPCD , OAQPS	30 days after the activity	RAVL
DQAs	1/yr	RAVL and OAQPS	120 days after the end of calendar year	OAQPS, RAVL
PE	1/yr	RAVL, NIST	30 days after the activity	RAVL

[3] American National Standard-Quality Systems for Environmental Data and Technology Programs-Requirements with Guidance for Use (ANSI/ASQC E4-2004)

21.0 Reports to Management

This element describes the quality-related reports and communications to management necessary to support the AA-PGVP. For the AA-PGVP, management is considered the supervisors of the RAVL, the OAQPS AA-PGVP Lead and members of the AA-PGVP Advisory Group.

21.1 Tracking Report

Upon completion of a quarters verification, the AA-PGVP Tracking Form, described in Section 19 will be posted on AMTIC. This form does not provide results of the verification but does provide an assessment of progress of the program.

21.2 Audit Reports

Any TSA's or other official reviews or audits performed on the AA-PGVP will be provided to management. Audits are discussed in Section 20.

21.3 Individual Producer Results

OAQPS is responsible for notifying each participating producer about whether the RAVLs measurements differ by more than +/- 2.0 percent from the producer's corresponding certified concentrations. OAQPS will not indicate the measured concentrations that the laboratory has determined nor whether the RAVL measured values are lower or higher than the certified value. It will notify each producer separately. The verification results for a specific producer will not be shared with anyone but that producer.

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.

21.4 Initial Draft Verification 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 organizations. At a minimum, the draft verification results shall include:

(a) a description of the gas metrological techniques, analytical method and analytical instrumentation, and the statistical procedures that were used in the calculation of the measured concentrations and their estimated total uncertainties;
(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.

21.5 Final Verification Results

Upon receipt of the final verification results from the RAVL, OAQPS will publish and disseminate the verification (with appropriate caveats associated with how they should be interpreted) and the certificate inspection results.

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 will post the results on the AMTIC website. The website will include results from the most recent verification as well as the verification results from previous years. EPA may prepare papers concerning the final verification results for presentation at professional meetings and for publication in the professional literature.

21.6 AA-PGVP QA Report

The report will provide a summary of the QA information related to the AA-PGVP. It will summarize QC data from all the runs with respect to achieving the MQOs as well as aggregating QC data from the runs to provide overall data quality statistics for each RAVL. It will summarize any external assessments (TSAs or PEs) that were performed, the audit results and findings, and any corrective actions that were needed. It will provide lessons learned and improvements needed for the following year.

22.0 Data Review, Validation, and Verification Requirements

This element describes how the AA-PGVP will verify and validate the data collection operations associated with the program. “Verification” can be defined as confirmation by examination and provision of objective evidence that *specified requirements* have been fulfilled. “Validation” can be defined as confirmation by examination and provision of objective evidence that the particular requirements for a specific *intended use* are fulfilled. The major objective for the AA-PGVP is to provide data of adequate quality to use in the comparison of the specialty gas producer standards. This section will describe the verification and validation activities that occur during a number of the important data collection phases. Earlier elements of this QAPP and the AA-PGVP Laboratory SOPs describe how the activities in these data collection phases will be implemented to meet the DQOs of the program. Review and approval of this QAPP provide initial agreement that the processes described in the QAPP, if implemented, will provide data of adequate quality. To verify and validate the phases of the data collection operation, the AA-PGVP will use various qualitative assessments (e.g., technical systems audits etc.) to verify that the QAPP is being followed and will rely on the various laboratory QC samples to validate the measurement process.

22.1 Verification/Validation of Sample Handling

Section 12.0, *Sample Handling and Custody*, detail the requirements for sampling handling. As mentioned in the above section, TSAs will be performed to ensure that the specifications mentioned in the QAPP and SOPs are being followed. The assessments would include checks on the identity of the sample, proper labeling and COC records and proper storage conditions to ensure that the standards from shipping through analysis and back to the monitoring organization are being achieved as required.

22.2 Analytical Procedures-Verification/Validation Through the AA-PGVP Data Workbook

Section 13.0, *Analytical Methods Requirements,* details the requirements for the analytical methods. The verification/validation process for the AA-PGVP is fairly simple. If the QC acceptance criteria is achieved and the RAVLs analyze their laboratory’s NIST SRMs within the acceptance range, then one can expect that the derived concentrations of the specialty gas standards are acceptable.

As explained in Section 19, the RAVL will use the MDW explained in Appendix A of the *Protocol Gas Document.* The MDW provides for entry of the calibration, zero/span, SRM and candidate cylinder information and provides the calculations to determine acceptable results (Table 19-1). If results for either the QC criteria or the candidate cylinders do not make acceptance criteria the RAVL will re-run the analysis. If the QC data are acceptable for both the first and second runs but the candidate cylinder(s) do not meet the acceptance criteria (against their certified value) the RAVL will assume it is the gas producers cylinder and not the analysis.

Monitoring organizations will receive results of verifications within 3 weeks of the analysis. If results are outside the acceptance windows, 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

If a specialty gas 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, then the producer 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.

The following validation functions are incorporated into the AA-PGVP to ensure the quality of data entry and data processing operations:

- **100% data review.** COC and MDW are subjected to a 100% data review by the RAVL laboratory analyst and random reviews once a month by the AA-PGVP Laboratory Manager or designated Laboratory QA Officer.
- **Completeness checks.** When the data are processed, certain completeness criteria must be met. At a minimum, COC Forms, and all data on the MDW must be completed to ensure accurate results.
- **Data retention.** Raw data sheets are retained in the laboratory files for a minimum of 4 calendar years and are readily available for audits and data verification activities. After 4 years, the FS or LA may request instructions from OAQPS on the disposition of hard copy records and computer back-up media.
- **Statistical data checks.** Errors found during statistical screening using the MDW will be traced back to original data entry files and to the raw data sheets, if necessary. These checks shall be conducted on a monthly schedule and before any data are submitted to the AQS.

Table 22-1 summarizes the validation checks applicable to the AA-PGVP data.

Table 22-1. Validation Check Summaries

Type of Data Check	Electronic Transmission and Storage	Manual Checks	Automated Checks
Data parity and transmission protocol checks	✓		
Data review		✓	
Date and time consistency		✓	✓
Completeness of required fields		✓	✓
Range checking			✓
Manual inspection of charts and reports		✓	
Sample batch data validation			✓

23.0 Reconciliation with Data Quality Objectives

For the data from the AA-PGVP to be used for comparing the measured concentration against the certified concentration, the data must be internally consistent, meaning that the data should be precise and unbiased. Element 7.0, *Data Quality Objectives and Criteria for Measurement*, of this QAPP contains the details for the development of the DQOs and the MQOs. Due to the nature and use of the data, all MQOs in Table 7-1 will be achieved before the gas standard measured concentration data will be considered acceptable. Achievement of the MQOs will provide reasonable assurance that the measured concentration of the gas standard is precise and unbiased (within acceptable ranges of the MQO). Achievement of the MQOs will allow EPA to determine whether or not the standard concentration is within ± 2% of the certified value.

Appendix A

Ambient Air Protocol Gas Verification Program
Participation Survey

This Survey would be sent to all Ambient Air Monitoring Organizations currently submitting data to AQS. It provides EPA with information on:

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

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DRAFT

AA-PGVP Monitoring Organization Survey Calendar Year 2010

PQAO Name: ________ PQAO Code ________

Reporting Org Name: ________ Reporting Org. Code ________

Point Of Contact ________ POC Email ________

	Specialty Gas Producers Name	Address City	State	Producer Code
Primary				
Secondary				
Other				
Other				

Do you plan on purchasing gasses in the next 12 months? Y/N ________ Approximate month of purhase ________

Pollutants Planned on Purchasing

					Y/N
Pollutant		Concentration		Multiblend?	
Pollutant		Concentration		Multiblend?	
Pollutant		Concentration		Multiblend?	
Pollutant		Concentration		Multiblend?	
Pollutant		Concentration		Multiblend?	

Would you be willing to participate in the PGVP? Y/N ________

Is your Org. trained/ certified to ship gas cylinders?** ________

** Per 49 CFR Part 172.704 Training requirements for shipment of hazardous material

Appendix B

Ambient Air Protocol Gas Verification Program
Chain of Custody Form

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DRAFT

Ambient Air Protocol Gas Verification Program 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	SO_2 (ppm)	NO (ppm)	CO_2 (%)	O_2 (%)	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

Standard Operating Procedures for the Verification of NO/NOx, SO2, and CO Concentrations in EPA Protocol Gas Mixtures

Region 2 (1-109)
Region 7 (1-110)

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Standard Operating Procedures for the Verification of NO/NOx, SO2, and CO Concentrations in EPA Protocol Gas Mixtures

Avraham Teitz – EPA Region 2
Thien Bui – EPA Region 7

March 12, 2010

Approved:

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Avraham Teitz, US EPA Region 2

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Thien Bui, US EPA Region 7

____
Michael Papp, OAQPS

____
XXXXXXX, OAQPS

Page

2.0 Purpose

The purpose of this procedure is to verify the concentration of CO, SO2, NO, and NOx in gas standards purchased by State, Local and Tribal monitoring agencies that have been certified by the gas vendor as meeting the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121).

3.0 Scope

This document is an adaptation of the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) using the specific equipment, tools, and resources available to the Region 2 Ambient Monitoring Standards Laboratory. This document is designed for use by trained air monitoring personnel in order to assure consistent laboratory practices in the verification of CO, SO2, NO, NOx concentrations in cylinder standards designated by the gas vendor as meeting the EPA Protocol referenced above. Untrained users, familiar with good laboratory practices, may also find this a useful guide, although specific air monitoring knowledge is assumed by the authors.

4.0 SOP Availability

This SOP shall be available as a reference in the Ambient Air Monitoring Standards Laboratory work area during the course of all verification of EPA Protocol Gases by EPA Region 2, as well as the Monitoring and Assessments Branch Master File of Ambient Air Monitoring SOPs located in the G:\User\DESA\MAB\AWQAT\Ambient Air Monitoring\SOPs folder on the Regional Computer Server.

5.0 Revisions

This SOP shall be reviewed annually to ensure that the policies and procedures remain current and appropriate. The SOP will be modified whenever the calibration procedures are changed.

6.0 Inherently Governmental Functions

This method is to ensure compliance with 40CFR Part 58 Appendix A, Section 2.6 which requires gas vendors to participate in an EPA Protocol Gas Verification Program. As such this program is an inherently governmental function.

7.0 Definitions

SRM = Standard Reference Material, obtained from NIST
NIST = National Institute of Science and Technology

G2 Protocol = Portion of the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) pertaining to assay of gas with dilution of reference and candidate standards.

Protocol Gas = a compressed gas cylinder assayed by the vendor according to the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121).

Analyzer = EPA reference and equivalent analyzers. In this particular SOP it refers to either a Thermo 48C or 48i (CO), Thermo 42i (NO/NOx), or Thermo 43i (SO2).

CO = Carbon Monoxide
SO2 = Sulfur Dioxide
NO = Nitrous Oxide
NO2 = nitrogen dioxide
NOx = Oxides of Nitrogen
Calibrator = A gas phase titration calibrator, such as a Environics 6103
Zero Air = diluent gas free of contaminants
Candidate cylinder = a protocol gas cylinder under test for assay.
MFC = Mass Flow controller, found in the calibrator
Laboratory Primary Flow Standard= BIOS ML-800 (Region 2), BIOS DC-Lite/Definer (Region 7)
Primary Standard = An NIST SRM gas cylinder (NO/NOx, SO2, or CO)
Check Standard = A NIST SRM gas cylinder (NO/NOx, SO2, or CO) at a different concentration than the primary standard
URL = Upper Range Limit of an ambient air analyzer

8.0 Safety Warnings

This SOP requires the use of compressed gas cylinders under high pressure (150-2000 psig). Therefore, cylinder handling safety is of primary importance. Cylinders must be capped while moving and secured with appropriate restraints during use. Pressure regulators should be properly tightened before cylinder valves are opened. Make certain that the pressure regulator is adjusted so that equipment downstream will not be pressurized above anticipated values.

This procedure makes use of cylinder gases at the following concentrations; CO at 2500-10,000 ppm for diluted standards and 40-50 ppm for undiluted standards, and NO/NOx and SO2 at 25-100 ppm. Gases at delivery are at the following concentrations; CO at 25-50 ppm, and NO and SO2 at 250-500 ppb. Since excess gas at delivery is required, make sure that adequate ventilation and/or exhaust manifolds are present when using this procedure.

9.0 Procedural Cautions

The 1/8” tubing that is connected to the cylinder can easily crack if abused or twisted. This failure is not always easily seen, particularly when the break occurs at the fitting nut. Significant loss of SRM gas will result. If the cylinder valve is left open at the end of the day, even if the regulator outlet is shut, significant losses of SRM may occur in the ensuing days/weeks until it is used again. SRM gas is expensive and difficult to obtain. **Regularly check the cylinder pressure levels while the cylinder is in use, so that any leaks may be quickly repaired. Check and double check all cylinder valves at the end of the day to be certain that the SRM cylinder is closed**.

NO/NOx and SO2 analysis require an equilibrated regulator that has been pressurized overnight with gas. Failure to do so may result in long equilibration times and potentially inaccurate or variable results.

The SO2 assay requires a considerable amount of time (45 minutes – 1 hour) to reach equilibration during the first span point of the day, particularly if the gas handling system (cylinder/tubing/calibrator/analyzer/manifold) has not been used to generate upscale points in the previous 24 hours. Treat the equilibration times given in this procedure as minima, and observe them scrupulously, as the accuracy of the assay is dependent on it.

10.0 Summary of Method

The EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) G2 methodology will be followed. As implemented, a mass flow controlled gas calibrator will be used to dilute either a NIST Standard Reference Material (SRM) or a State/Local provided EPA Protocol gas. The resulting diluted gas will be analyzed using an EPA reference or equivalent ambient air analyzer. Flow calibrations will be based on a BIOS ML-800 primary flow standard.

11.0 Apparatus and Materials

NIST SRM 2639a CO @ 10,000 ppm
NIST SRM 2638a CO @ 5,000 ppm
NIST SRM 1694a SO2 @ 100 ppm
NIST SRM 1693a SO2 @ 50 ppm
NIST SRM 1684a NO @ 100 ppm
NIST SRM 1683b NO @ 50 ppm
Thermo 48C (or 48i) CO analyzer
Thermo 43i SO2 analyzer
Thermo 42i NO/NOx analyzer
Environics 6103 gas phase titration calibrators
BIOS ML-800 (Region 2 Laboratory or BIOS DC-Lite/Definer (Region 7 Laboratory)
Primary flow standard with 0-30 liter cell and 0-500 cc cell
Four stainless steel CGA 660 regulators for SO2/NOx analysis
Two brass CGA 350 regulators for CO analysis
House zero air gas supply sufficient for 20 L/minute

Envidas computer data acquisition system
50 feet of ¼” o.d. thick walled Teflon tubing
50 feet of 1/8” o.d. thick walled Teflon tubing
¼” and 1/8” Swagelok nuts and ferrules
Calculations spreadsheet from EPA Protocol (EPA-600/R-97/121), 9/1997 edition
Computer
Protocol Gas Verification Program Working Instructions for CO, SO2, and NO/NOx
Laboratory logbook

12.0 Preparation

All NIST SRMs and the ML-800 must be within their certification dates. The analyzer, calibrator, and cylinder regulator must be equilibrated prior to commencement of this assay. Ideally, all equilibration should start the night before and include:

Powering up of the calibrator, zero air supply, and analyzer.

Supplying the analyzer with zero air at a sufficient flow volume such that excess air is drawn into the exhaust manifold. In our case the accepted volume is 3 liters/minute.

Pressurizing the regulator

Failure to equilibrate the regulator can result in lengthy equilibration times, on the order of 2 to 3 hours. Failure to adequately equilibrate the analyzer and calibrator can result in lengthy equilibration delays as well as erroneous results. Detailed information on these requirements and procedures may be found in the working instructions, which are presented in the Appendices.

13.0 Procedure

The procedure for assay is presented in exhaustive detail in the working instructions for CO, SO2, and NO/NOx in the Appendices. Presented below is an outline of the procedure:

13.1 Flow Calibration of Environics 6103 Calibrators

Environics 6103 calibrators, used for dilution of zero and reference/candidate standards, will have their mass flow controllers calibrated within 2 weeks of any assay utilizing a BIOS ML-800 primary standard that has been certified by an NVLAP Laboratory.

13.2 Analyzer Calibration

CO, SO2, and NO/NOx ambient air analyzers will be calibrated from 50% to 90% of their upper range limit (URL). This is the most accurate range for these analyzers. Analyzers must be calibrated within 2 weeks of any assay.

13.3 Calibrator Dilution Check

The quarterly calibrator dilution check procedure are specified in detail, in the in the working instructions presented in the Appendices. The dilution check consists of: 1) multipoint calibration of the ambient air analyzer as stated in Section 13.2, utilizing a 10,000 ppm CO SRM, followed by 2) generation of 3 discrete points >80% of the instrument URL with the same calibrator using a NIST CO SRM with a concentration of 5000 ppm. The acceptance criteria for the predicted response versus the analyzer response with the 5000 ppm standard is a relative percent difference of <1%. Calibrator dilution checks must be conducted within 2 weeks of any assay.

13.4 Day of Assay Zero, Span, and Precision Check of Ambient Air Analyzers

On the day of each assay, each ambient air analyzer will be checked for precision and drift with 3 discrete analysis of a NIST SRM at a concentration of >80% of the instrument URL. Calculations of acceptability for these parameters will be done using the spreadsheets from the EPA Protocol method. The exact procedure is found in the working instructions presented in the Appendices.

13.5 Assay Gases

Gases accepted for assay must:

1. Have the concentration of gas certified by the vendor in accordance with the EPA-600/R-91/121 EPA Traceability Protocol.

2a. Contain CO at concentration ranges of 2500 – 10,000 ppm (for CO dilution standards) or 40-50 ppm (for direct CO standards), or

2b. SO2 and NO/NOx at concentrations of 25-100 ppm.

2c. Balance gas will be nitrogen.

3. Each cylinder accepted for assay must be accompanied with a copy of the original written certification report.

13.6 Assay Procedure

All assays of reference and candidate standards will be analyzed in 3 test sets, with each set consisting of all of the candidates standards, the primary SRM, and zero gas.

Cylinders will be run in a different order for each test set. All adjustments in dilution flow will be done with the diluent gas mass flow controller of the dilution calibrator. The pollutant mass flow controller will be set to a constant flow of 70 cc/min, with the exception of zero gas runs, where it will be set to 0.0 cc/min. Delivered gas concentrations will be >80% of the ambient air analyzers URL. Exact details of the assay procedure are presented in the working instructions, presented in the Appendices.

13.7 Quality Assurance Requirements

A table of the Quality Assurance requirements is presented below:

QA Parameter	QA Requirement
SRM Gas Standards (primary and check)	SRM certificate is not expired SRM pressure > 150 psig
Laboratory Flow Standard	Certified by NVLAP certified laboratory Certification is not expired
Dilution Calibrator	Flow calibrated within 2 weeks of assay Dilution check within 2 weeks of assay Flow error after calibration < 1%
Ambient Air Analyzer	Calibrated within 2 weeks of assay Estimate of Uncertainty <1% for assay range Analyzer calibration slope 0.98 - 1.02
Calibrator Dilution Check	Dilution check within 2 weeks of assay Dilution Check relative % difference <1%
Day of Assay Zero, Span, and Precision	Zero Check standard error <1% Zero Check accuracy within 5% Span standard error <1% Span accuracy within 5%
Candidate Standards	Standard error of assay <1% Error relative to vendor certificate <2% = acceptable Error relative to vendor certificate 2-4% = caution Error relative top vendor >4% = exceeds program limits

A detailed QA table is presented in the working instructions, presented in the Appendices

14.0 Calculations

The assay method as implemented consists of the written instructions and their accompanying EXCEL spreadsheets. All cylinder concentration calculations use the original worksheets developed for the EPA Protocol. Additional worksheets were added to the original protocol method to facilitate the quality assurance checks and procedural requirements in the EPA Protocol. Detailed instructions for using these worksheets is presented in the working instructions in the Appendices.

15.0 Data Reporting

There are 3 EXCEL workbooks, one for each pollutant; PGVP-CO, PGVP-SO2, and PGVP-NO/NOx. These workbooks are an integral part of the assay, and they are tightly integrated with the assay working instructions. The workbooks are the repository for all assay information, assay results and quality assurance information, Data will be reported from the analytical laboratory, via these worksheets, directly to OAQPS, which will disseminate this information to monitoring agencies providing gas cylinder standards for assay.

16.0 References

The EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121)

Working Instructions For Carbon Monoxide Assays For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

Working Instructions For Sulfur Dioxide Assays For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

Working Instructions For Oxides of Nitrogen For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

PGVP-CO EXCEL Workbook

PGVP-SO2 EXCEL Workbook

PGVP-NOx EXCEL Workbook

APPENDIX A:

WORKING INSTRUCTIONS

FOR

CARBON MONOXIDE ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 2

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Monitoring Management Branch
US EPA Region 2
2890 Woodbridge Avenue
Edison, NJ 08837

Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-CO v3.1.xls.** When using and/or archiving the PGVP-CO Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_C_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 -XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for CO data.

2.0 Assay Information Worksheet

The PGVP-CO Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: Flow calibrations are required within 2 weeks of any PGVP assay.

3.1 Materials Required

a. Environics 6103 Multi-gas Calibrator with 20 L/min diluent and 100 cc/min pollutant mass flow controllers (**MFC**s).

b. Filtered and pressure regulated air source capable of delivering 20 L/min at 30 psig. The air source must be capable of delivering flow to 2 ports at the same time.

c. BIOS ML-800 w/Model #44 (0-30 L/min) and #10 (5-300 cc/min) flow cells and 9 pin data cable.

d. Laptop computer with Excel and BIOS Optimizer flow program and appropriate PGVP-xx workbooks.

e. Wrenches, 9/16” and 7/16” for working with ¼” and 1/8” Swagelok fittings.

f. ¼” Teflon tubing, 4’ length and terminated by ¼” Swagelok nut.

g. 1/8” Teflon tubing, 3’ length and terminated by a 1/8” Swagelok nut at one end. The other end is attached to a 2’ length of ¼” tubing via a Swagelok reducing union, and terminated by ¼” Swagelok nut.

h. ¼” and 1/8” Swagelok nuts, ferrules, and tee.

i. Phillips and flathead screw drivers.

j. Laboratory countdown timer.

k. Laboratory logbook and pens.

3.2 Environics 6103 Calibrator Setup and Gas Connections

3.2.1 Connect the outlets of the compressed air supply to **PORT 1** and **PORT 2** on the back of the calibrator. The air should not be turned on at this time.

3.2.2 Ensure that at least one of the **MANIFOLD OUTLET PORTS** is open to atmosphere.

3.2.3 Open the top lid of the Environics 6103 by removing the 4 screws on the top (the 2 screws on each of the side panels have been permanently removed), and lift the lid off the instrument.

3.2.4 On the right side panel, remove the rightmost and leftmost Phillips head screws. The right side panel will now open, as the bottom is hinged. Lay the right side panel down as flat as it goes.

3.2.5 Locate the diluent MFC. There are two MFC's located in the right front quadrant of the instrument. The diluent MFC can be identified by its position closer to the center and front of the instrument and the use of ¼" fittings. The MFC inlets are towards the rear of the instrument, and the outlet is toward the front.

3.2.6 Using a 9/16" wrench, remove the nut to the outlet of the diluent MFC.

3.2.7 Connect a 4' piece of ¼" Teflon with Swagelok nuts and ferrules to the diluent MFC outlet.

3.2.8 Turn on the Calibrator.

3.2.9 Turn on the compressed air supply to deliver 30 psi.

3.2.10 At the bottom of the LCD display, there will be 3 labels,

CONC FLOW PHOTO

directly above the 3 function switches (**F1, F2, F3**). Push **FLOW** (button **F2**).

3.2.11 Three new labels will appear on the bottom of the LCD Panel

START GAS EXIT.

Push **START** (button **F1**).

3.2.12 Three new labels will appear on the bottom of the LCD Panel

EDIT VIEW STOP.

Push **EDIT** (button **F1**).

3.2.13 Three new labels will appear on the bottom of the LCD Panel

UPDATE VIEW STOP.

The cursor will default to the top line, **AIR=0.0000 lpm**. On the keypad, enter 16.0.

3.2.14 Using the front panel arrow keys, move the cursor one row down to **CO=0.0000 ccm**. Enter 78.0 on the numerical keypad and push **UPDATE** (button **F1**). The calibrator will accept the changes and return to the display seen in section 3.2.12.

Note: The Environics 6103 has a solenoid that cuts off all flow to both MFCs if there is no pressure at the diluent flow controller. Therefore, there must be flow present at the diluent MFC at the same time in order for zero air to flow to the pollutant gas flow controller, thus requiring the need for 2 compressed air inputs.

3.2.15 The front panel LCD should now indicate flow for both MFCs. Press **MENU** on the front panel. The LCD display will show:

O3 CONTROL = DISABLED
PHO SOURCE = EXTERNAL
PHO PUMP = OFF
O3 CTRL PHOSRC PUMP

Front panel buttons F1, F2, or F3 correspond to the parameters of O3 control, photometer source, and the photometer pump, respectively. If the display does not show the parameters shown above, push the function button corresponding to the parameter that needs correction and toggle it to the correct value. Push the **MENU** button to accept these changes and go back to the default run display.

Note: The screen for O3 control, photometer source, and the photometer pump can only be called up after pressing START, as was done in step 3.2.11.

3.2.16 Let the calibrator equilibrate for a minimum of one hour prior to taking measurements.

3.3 BIOS ML-800 Setup and Flow connections

3.3.1 Put the high flow cell (cell #44) on the ML-800 base. Open the inlet and outlet caps of the cell.

3.3.2 Plug in the ML-800 to the wall outlet and press **ON**.

3.3.3 The front panel will display:

Run
Setup
Leak Test

Using the arrow keys on the front panel, toggle the cursor one step down to **SETUP** and press enter.

3.3.4 The LCD display will show:

Setup Menu – 1
Sensor Factor = 1.000
Cal. Type Std.

If the **Sensor factor** or the **Cal. Type** do not read these values, consult the ML-800 Manual, Chapter 8.0, to adjust these parameters to these values.

3.3.5 Push the right arrow on the front panel (**FWD**). The LCD display will show:

Setup Menu – 2	
Reading Type	**Cont**
# in avg.	**50**
Min/Reading	**00**

The critical parameter here is **Reading Type Cont**, as this will allow the ML-800 to operate continuously. If the setup menu indicates **Reading Type Burst**, move the cursor one row down (**DOWN** arrow on the front panel) to the **Reading Type** line and press **ENTER**. The cursor will move under **Cont**. Press the **UP** arrow on the front panel to toggle **Burst** to **Cont**, and press **ENTER**.

3.3.6 Push the right arrow on the front panel (**FWD**). The LCD display will show:

Setup Menu – 3	
Press Units	**mmHg**
Temp Units	**^{o}C**
Temp Corr	**25.00**

If these parameters are not set to the readings above, move the cursor to the affected line, press **ENTER**. This will move the cursor to the setting to be changed. Enter the correct settings shown above, and press **ENTER** again to accept the changes.

3.3.7 Push the right arrow on the front panel (**FWD**) 4 more times to scroll through setup menu pages 4 through 6, and to arrive at the original display screen of

Run
Setup
Leak Test

3.3.8 The cursor will default to the **Run** line. Press **ENTER**. Confirm that the bottom right hand side of the display shows **ST=25.0** and **SF=1.000**. ST refers to the standard temperature and SF refers to the sensor factor. If ST and SF are not as indicated above, change it in the setup menu as outlined in steps 3.3.4 - 3.3.7 above. The instrument is now ready for use.

3.3.9 Connect the tubing attached to the Environics 6103 diluent MFC output to the Swagelok fitting on the left hand side of Cell #44.

3.3.10 Press the **AUTO** button on the ML-800 front panel. The piston will start to move, and the ML-800 will display start to display flow readings.

3.4 Computer Setup and Data Logging for Flow Calibration

3.4.1 Connect the 9 pin data cable to the BIOS ML-800 and the laptop computer.

3.4.2 Start the computer, and launch the BIOS Optimizer program.

3.4.3 Click on the LOGIN icon in the upper left hand corner of the program. The user and password window will open.

3.4.4 Enter **biosadmin** for the user name and **bios** for the password. Use lower case for entering the information.

3.4.5 In the DATA STREAM FILE LOCATION window at the top of the program enter **C:\BIOS data\YYYY-MM-DD PGVP Environics 6103.txt**, where **YYYY-MM-DD** denotes the date of calibration in year-month-day format.

3.4.6 Press the **start** button in the Optimizer program. Data will be collected and a chart will be generated in the program showing all data points collected.

3.4.7 Start a new page in the PGVP laboratory logbook and enter the current date and time, and a heading of "Environics 6103 flow calibration".

3.5 Environics 6103 Diluent MFC Calibration

Note: The Environics 6103 calibrator must be warmed up at 16 L/min for the diluent flow and 78 cc/min for the pollutant flow for 60 minutes prior to the start of the calibration per the instructions in section 3.2. The ML-800 flowmeter should already be collecting data for the diluent flow controller as per section 3.4.

3.5.1 Ensure that the Environics 6103 diluent MFC is set to 16.0 L/min. Set the timer for 20 minutes and wait until the timer indicates that the time has elapsed.

3.5.2 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement) press **STOP** on the Optimizer data program**.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.2.

3.5.3 Set the flow of the Environics 6103 diluent MFC to 12.0 L/min. Setting of flows has been specified in section 3.2.

3.5.4 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.5.5 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.5

3.5.6 Set the flow of the Environics 6103 diluent MFC to 8.0 L/min.

3.5.7 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.5.8 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.8.

3.5.9 Set the flow of the Environics 6103 diluent MFC to 6.0 L/min.

3.5.10 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.5.11 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.11.

3.5.12 Set the flow of the Environics 6103 diluent MFC to 4.0 L/min.

3.5.13 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.5.14 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 2.5.14. This is the last measurement for the diluent MFC.

3.5.15 Detach the 4' Teflon line from the ML-800 and the diluent MFC output and reattach the Environics ¼" fitting removed in step 2.2.6 to the output of the diluent MFC.

3.6 Environics 6103 Pollutant MFC Calibration

3.6.1 Remove the 1/8" Swagelok fitting from the pollutant MFC output. The output is found on the end of the pollutant MFC closer to the front panel of the calibrator.

3.6.2 Locate the 1/8” tubing referred to in step 2.1. Attach the 1/8” nut to the output of the pollutant MFC.

3.6.3 Replace BIOS cell #44 (0-30 L/min) with Cell #10 (0-300 cc/min) on the ML-800 base unit.

3.6.4 Cap the inlets and outlets of BIOS cell #44, and remove the inlet and outlet caps on cell #10.

3.6.5 Attach the tubing from the pollutant MFC outlet to the inlet fitting of cell #10 (left hand side fitting).

3.6.6 Move the cursor of the ML-800 LCD panel to **RUN** and push **ENTER** on the ML-800 front panel. The piston will start to move as a flow rate of 78 cc/min was programmed for the pollutant MFC previously in step 3.2.14. Push **RESET** on the ML-800 front panel to reset the flow average.

3.6.7 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.6.8 If a stable trace has been established, press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.8.

3.6.9 Set the flow of the Environics 6103 pollutant MFC to 70.0 cc/min.

3.6.10 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.6.11 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.11.

3.6.12 Set the flow of the Environics 6103 pollutant MFC to 60.0 cc/min.

3.6.13 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.6.14 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.14.

3.6.15 Set the flow of the Environics 6103 pollutant MFC to 50.0 cc/min.

3.6.16 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.6.17 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. Push **RESET** on the ML-800 front panel to reset the flow average. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.17.

3.6.18 Set the flow of the Environics 6103 pollutant MFC to 40.0 cc/min.

3.6.19 Set the timer for 20 minutes and push **AUTO** on the ML-800 front panel.

3.6.20 If a stable trace has been established press **STOP.** Record the Environics set point, reading, and the average flow as indicated in the LCD panel of the ML-800, in the laboratory logbook. If a stable reading has not been achieved, push **RESET** on the ML-800 front panel to reset the flow average and reset the timer for 20 minutes and repeat step 3.6.20. This is the last point in the pollutant MFC calibration.

3.6.21 Detach the Teflon line from the ML-800 and the pollutant MFC output and reattach the Environics 1/8" fitting removed in step 3.6.1 to the output of the diluent MFC.

3.6.22 Replace the lid of the Environics 6103 and reattach the 4 screws that were removed in step 3.2.3.

3.7 Flow Calculations/Completion of the Calibrator Flow Cal Worksheet

Note: Flow calibrations of the Environics 6103 by default utilize the PGVP-CO workbook. For SO2 and NO/NOx assays the data collected in this worksheet is copied and pasted into the respective PGVP-SO2 and PGVP-NOx workbooks. Copying and pasting procedures are given in the respective SO2 and NO/NOx, workbooks.

3.7.1 In the PGVP-CO workbook, open the Calibrator Flow Cal worksheet.

3.7.2 Data collected during the flow calibration must be transferred to the Calibrator Information block. Click the **DATA** tab on the top Excel menu bar, scroll down the drop down menu to **IMPORT EXTERNAL DATA**, and highlight **IMPORT DATA**. The **SELECT DATA SOURCE** window will open.

Note: If the IMPORT DATA window is grayed out, it is because the source data definitions from a previous use are still defined. To clear this select DATA → IMPORT EXTERNAL DATA → DATA RANGE PROPERTIES. This will open up

the EXTERNAL DATA RANGE PROPERTIES window. Uncheck the box SAVE QUERY DEFINITION. This will open a dialog box requesting to permanently delete the query definition. Click OK. This will close the dialog box. Then click OK on the EXTERNAL DATA RANGE PROPERTIES WINDOW. Now you can restart at the beginning of this step to import data.

3.7.3 In the **SELECT DATA SOURCE** window, click on the drop down menu at the top and highlight the file previously selected for storing the BIOS flow data in section 3.4.5 (**C:\BIOS data\XXXX-XX-XX PGVP Environics 6103.txt**). The **TEXT IMPORT WIZARD STEP 1 OF 3** window will open.

3.7.4 Select the **DELIMITED** radio button. The other defaults, **START IMPORT AT ROW 1** and FILE **ORIGIN 437: OEM United States**, should be left as is. In the lower half of the window will be the path length to the selected file as well as a limited preview of the file selected.

3.7.5 Click the **NEXT** button. The TEXT **IMPORT WIZARD STEP 2 OF 3** window will open.

3.7.6 In the **DELIMITER** block put a check mark by the **COMMA** field. Uncheck any other selected delimiters.

3.7.7 Click **NEXT**. The **TEXT IMPORT WIZARD STEP 3 OF 3** window will open.

3.7.8 Click **FINISH**. The **IMPORT DATA** window will open.

3.7.9 In the **IMPORT DATA** window, the **EXISTING WORKSHEET** radio button should be highlighted (this is the default) and the window below it should already be highlighted and read **=$A$1**. Enter **=$M$48** in the highlighted window and click **OK**. The window will close and the BIOS flow data will be imported into the Calibrator Flow Cal worksheet starting at cell M48.

3.7.10 The Calibrator Flow Cal worksheet consists of 4 blocks. In the first block, Calibrator Information, enter the calibration date and any notes. These fields are highlighted in yellow. The other fields in this block, Manufacturer, Model #, and Serial # will automatically be filled in, as these data are carried over from the Assay Information worksheet. The yellow highlighted fields are exported automatically to the Assay Information worksheet, in the Gas Dilution Calibrator block.

3.7.11 The second block in the Calibrator Flow Cal worksheet is Flow Standard Information. All the blocks should already be filled in, as the information is obtained from the Assay Information worksheet automatically.

3.7.12 The third block in the Calibrator Flow Cal worksheet is Flow Calibration. The calibration date in the header of this block is taken automatically from cell B5. Enter the set points and Environics 6103 readings obtained for the diluent MFC into cells B20..B24 and C20..C24, respectively. These data were recorded in the laboratory logbook in section 3.5 above.

3.7.13 Enter the set points and Environics readings obtained for the pollutant MFC flow into cells G20..G24 and H20..H24, respectively. These data were recorded in the laboratory logbook in section 3.6 above.

3.7.14 Place the cursor on, and highlight, cell D20, the first entry in the column for Actual Flow, and shaded yellow. Type the following formula:

=AVERAGE(Mxx..Myy)

Where: **xx** = is the last flow taken at 16.0 L/min
yy = the flow taken 10 minutes earlier

Hit **ENTER.** Cell row M is where the individual BIOS ML-800 flows were recorded. Cell Row Z shows the time the data point was taken. We are taking the average flow over the last 10 minutes of calibration.

3.7.15 Place the cursor on cell D21 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 12.0 L/min for **xx**, and the 12.0 L/min point taken 10 minutes earlier for **yy**.

3.7.16 Place the cursor on cell D22 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 8.0 L/min for **xx**, and the 8.0 L/min point taken 10 minutes earlier for **yy**.

3.7.17 Place the cursor on cell D23 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 6.0 L/min for **xx**, and the 6.0 L/min point taken 10 minutes earlier for **yy**.

3.7.18 Place the cursor on cell D24 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 4.0 L/min for **xx**, and the 4.0 L/min point taken 10 minutes earlier for **yy**.

3.7.19 Place the cursor on cell I20 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 78.0 cc/min for **xx**, and the 78.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.20 Place the cursor on cell I21 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 70.0 cc/min for **xx**, and the 70.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.21 Place the cursor on cell I22 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 60.0 cc/min for **xx**, and the 60.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.22 Place the cursor on cell I23 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 50.0 cc/min for **xx**, and the 50.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.23 Place the cursor on cell I24 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 40.0 cc/min for **xx**, and the 40.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.24 The Flow Calibration block will now show the slope and intercept for both MFCs.

3.7.25 The Curve Predicted columns in the Flow Calibration block are calculated by the formula:

CURVE PREDICTED VALUE = (MFC SETTING x SLOPE) – INTERCEPT

3.7.26 The % error in curve prediction is calculated by the formula:

(CURVE PREDICTED VALUE – ACTUAL FLOW)/(ACTUAL FLOW)

3.8 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 48C CO Analyzer Calibration Procedure & Analyzer Cal Worksheet

Note: The CO analyzer is set to a range of 50 ppm CO.

Note: The CO analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: The procedure for setting flow rates for Environics 6103 was described in section 3.2 and therefore will not be repeated here.

4.1 Required Materials

a. Thermo 48C ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 10,000 ppm CO SRM and CGA 350 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-CO workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to CO Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the ½" output line from the Environics 6103 to the glass CO manifold. The CO analyzers are by default plumbed to the glass manifold via ¼" Teflon lines. The exhaust of the manifold is vented via a ½" line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the CO manifold. Let the CO analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 48C CO analyzer(s).

4.2.6 Install the CGA 350 regulator on the 10,000 ppm CO SRM cylinder. The cylinder should be charged overnight according to the following procedure.

a. Turn the delivery valve of the pressure regulator to the closed position.

b. Turn the cylinder valve of the CO SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

c. Set the pressure regulator delivery pressure for 30 psi.

d. Close the cylinder valve. The pressure regulator will remain under pressure.

e. Check to verify that the SRM cylinder valve is closed.

f. Let cylinder and regulator equilibrate overnight.

4.2.7 Purge the CO SRM regulator according to the following procedure:

a. Attach a ¼" delivery line to the pressure regulator connected to the CO SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.2.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the CO SRM to Port 2 of the Environics 6103.

4.2.9 Open the CO SRM cylinder valve, and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Thermo 48C CO Analyzer Zero and Span

4.4.1 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 48C 10 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel and align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **BKG PPM** and **CO COEF** displayed on the Thermo 48C front panel in the laboratory logbook under the heading Thermo 48C Pre Calibration Background & CO Coefficient Readings. After taking the readings, push the **RUN** button on the Thermo 48C front panel.

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 48C display will show a new window with the cursor defaulting to the **CALIBRATE ZERO** line. Press **ENTER.** A new window will be displayed on the Thermo 48C displaying the current instrument reading and the question **SET TO ZERO?** Press **ENTER** a 2nd time to zero the instrument. After setting the zero, push the **RUN** button on the Thermo 48C front panel.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 16.0 L/min.

4.4.6 Allow the Thermo 48C to sample the Environics 6103 output for 15 minutes.

4.4.7 During this waiting period, open the Excel PGVP-CO Workbook that will be used for this batch of CO assays. The file naming conventions have been outlined in step 1.0. Open the Analyzer Cal worksheet and enter 16000 in cell B13, the High MFC Device Setting. Cell F13 will display the delivered CO concentration at the current conditions (Environics 6103 set for 16.0 L/min diluent and 78.0 cc/min pollutant gas using the 10,000 ppm CO SRM).

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4.4.8 After a steady trace is observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 48C display will show a new window with the cursor defaulting to the **CALIBRATE ZERO** line. Using the front panel arrow keys, place the cursor in front of the **CALIBRATE CO** line and press **ENTER.** A new window will be displayed on the Thermo 48C displaying the current instrument reading, analyzer range in ppm, and the line **SET TO 000XX.X00?** Using the arrow buttons on the front panel of the Thermo 48C, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered CO concentration specified in cell F13 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **RUN** button to get to the main screen of the Thermo 48C.

4.4.9 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.10 During the waiting period for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel, align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **BKG PPM** and **CO COEF** displayed on the Thermo 48C front panel in the laboratory logbook under the heading Thermo 48C Post Calibration Background & CO Coefficient Readings. After taking the readings, push the **RUN** button to return to the Thermo 48C main screen.

4.4.11 After a steady trace is observed , record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading Post Calibration Zero.

4.5 Thermo 48C Calibration for the CO Assay using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the Analyzer Cal worksheet from the Assay Info and Calibrator Flow Cal worksheets.

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4.5.1 In the Analyzer Cal worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 15 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G13 (analyzer response)of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G14 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 15 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G15 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 15 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G16 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 15 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G17 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G18 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

4.6.1 In the Analyzer Cal worksheet collect the delivered CO concentration and analyzer response: highlight cells F13..G18 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the calibration data for the CO analyzer into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F13 in the Analyzer Cal Worksheet (analyzer response) → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ copy. Go to the Analyzer Cal worksheet cell I13 → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F14..F17 (one cell at a time), recording the results in cells I14..I17, respectively.

4.6.7 The analyzer estimate of uncertainty must be less than 1% for the Thermo 48C to be considered well characterized at that concentration, and thus allowing the analyzer to be used for CO cylinder assays.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires 2 SRMs of different concentrations. For this method the 10,000 ppm CO SRM is referred to as the primary SRM and the 5,000 ppm CO SRM is referred to as the check SRM.

Note: The dilution check is done using the PGVP-CO workbook, Calibrator Dilution Check worksheet. If the Environics 6103 calibrator passes this check it is considered qualified for the SO2 and NO/NOX assays. Data from this sheet is then copied to the PGVP-SO2 and PGVP-NOX for their respective assays.

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

Note: The dilution check must be done with a CO analyzer that has been running for at least 3 hours, and preferably overnight sampling zero air. The CO SRM cylinders to be used should have equilibrated regulators as defined in section 4.2.6. The Environics 6103 calibrator should be warmed by running for at least an hour prior to starting this procedure.

5.1 Required Materials

This section requires all the materials enumerated in Section 4.1, plus a second CO SRM of 5,000 ppm (the SRM check standard)

5.2 Dilution Leak Check Procedure & Worksheet

5.2.1 Open the PGVP-CO workbook for the current assays and open the Calibrator Dilution Check workbook.

Note: All non shaded cells have their values automatically entered into the Calibrator Dilution Check worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

5.2.2 Enter the current date in cell B6, and any notes in cell I6.

5.2.3. Ensure that the ENVIDAS software is logging the Thermo 48C output data stream.

5.2.4 Set the Environics 6103 diluent MFC to 16.0 L/min.

5.2.5 Set the Environics 6103 pollutant MFC to 0.0 cc/min.

5.2.6 Connect the output of the Environics 6103 to the CO Glass manifold. The CO analyzer(s) are by default connected to this glass manifold.

5.2.7 Purge the regulator of the Primary CO-SRM, per the procedures outlined in section 4.2.7

5.2.8 Connect the output of the Primary CO SRM regulator to port 2 of the Environics 6103, and open the cylinder valve and regulator valve of the Primary CO SRM.

5.2.9 Set the Environics 6103 pollutant MFC to 70.0 cc/min and set the timer to 15 minutes.

5.2.10 During the waiting period, enter the diluent MFC flow rate (16,000), in cell D23 of the Calibrator Dilution Check worksheet.

5.2.11 After the timer has beeped, and a steady trace has been achieved (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), record the CO concentration from the ENVIDAS software 5 minute average in cell J23 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.12 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.13 During the waiting period, enter the diluent MFC flow rate (16,000), in cell D24 of the Calibrator Dilution Check worksheet.

5.2.14 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J24 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.15 Shut the regulator valve and then the cylinder valve of the Primary CO SRM. Disconnect the Primary CO SRM from Port 2 of the Environics 6103.

5.2.16 Purge the regulator of the Check CO SRM per the instructions in step 4.2.7..

5.2.17 Connect the check CO-SRM to port 2 of the Environics 6103 and open the cylinder valve and the regulator valve.

5.2.18 Set the Environics diluent MFC to 8.0 L/min, and the pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

5.2.19 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D25 of the Calibrator Dilution Check worksheet

5.2.20 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J25 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.21 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.22 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D26 of the Calibrator Dilution Check worksheet

5.2.23 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J26 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.24 Set the Environics pollutant MFC to 70.0 cc/min The diluent MFC should still be at 8.0 L/min.. Set the timer for 15 minutes.

5.2.25 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D27 of the Calibrator Dilution Check worksheet

5.2.26 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J27 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.27 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.28 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D28 of the Calibrator Dilution Check worksheet

5.2.29 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J28 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.30 Set the Environics pollutant MFC to 70.0 cc/min The diluent MFC should still be at 8.0 L/min.. Set the timer for 15 minutes.

5.2.31 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D29 of the Calibrator Dilution Check worksheet

5.2.32 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J29 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.33 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.34 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D30 of the Calibrator Dilution Check worksheet

5.2.35 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J30 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.36 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 70.0 cc/min. Set the timer to 15 minutes.

5.2.37 During the waiting period, enter the diluent MFC flow rate (16,000), in cell D31 of the Calibrator Dilution Check worksheet.

5.2.38 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J31 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.3 Calibrator Dilution Check Worksheet Evaluation

5.3.1 The Calibrator Dilution Check worksheet imports or calculates all data in the non shaded cells by obtaining the information from the Assay Information, Calibration Flow Cal, and Analyzer Calibration worksheets previously entered in the PGVP-CO workbook.

5.3.2 In order for the Environics 6103 to qualify for use in PGVP gas assays, the requirement from the EPA Protocol requires a relative % difference of < 1% calculated as follows:

$$\textbf{Relative \% difference} = (100)*\left(\frac{\text{mean analyzer Check SRM response} - \text{Predicted Response}}{\text{Predicted Response}}\right)$$

5.3.3 The mean response to the Check SRM is calculated in the Calibration Dilution Check worksheet in cell J32.

5.3.4 The predicted instrument response for the CO Check SRM is calculated in the Calibration Dilution Check worksheet in cell I26 (and I28 and I30), by determining the delivered CO concentration from the Environics 6103 settings and flow calibration and plugging this value into the Thermo 48C CO analyzer calibration results.

5.3.5 The calculation of relative % difference is given in cell D33 of the Calibration Dilution Check worksheet.

5.3.6 If the relative % difference is less than 1% the instrument has been qualified for use in CO, SO2, and NOx assays for a period of 2 weeks.

5.3.7 At the conclusion of this test, close all SRM gas cylinder valves, and run zero air through the Environics 6103 and the CO analyzer.

5.3.8 Save all data from the ENVIDAS data logging system and the PGVP worksheet.

6.0 Day of Assay Zero, Span, and Precision Procedure and Day of Assay Zero & Span Worksheet

Note: Standard Procedure in Region 2 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-CO workbook for the current assay and open the Day of Assay Zero and Span worksheet.

Note: All non shaded cells have their values automatically entered into the Day of Assay Zero and Span worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 48C output data stream.

6.2.3 Equilibrate the regulator on the Primary CO SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 48C must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary CO SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the carbon monoxide glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 16,000 in the High MFC Device Setting column in cells D17..D22.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J17 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J18 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J19 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J20 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J21 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J22 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Analysis Zero and Span Worksheet Finalization and Evaluation

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-CO Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

6.3.1 In the Day of Analysis Zero and Span worksheet, collect the response to zero gas: control-left click on cells J17, J19, and J21 → right click → copy.

6.3.2 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.3 Select the Day of Analysis Zero and Span worksheet, collect the predicted CO response: press escape → left click on cells H18 → control-left click on H20, and H22 → right click → copy.

6.3.4 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.5 Select the Day of Analysis Zero and Span worksheet, collect the analyzer CO concentration: press Escape → left click on cell J18 → control-left click on J20, and J22 → right click → copy.

6.3.6 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.3.8 Select the Day of Analysis Zero and Span worksheet → select cell D26 → right click → paste special → values → OK.

6.3.9 In the Day of Analysis Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D28 and D30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.10 In the Day of Analysis Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F28 and F30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.11 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 Carbon Monoxide Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary CO SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-CO workbook for the current assay and open the Assay Worksheet.

Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 48C output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 48C must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary CO SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 to the carbon monoxide glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 48C CO analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-50 ppm. With challenge standard cylinder concentrations of 2500 – 10,000 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart

Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
CO	10000	10,000	16.0	70	43.56
	5000	10,000	8.0	70	43.37
	2500	10,000	4.0	70	43.00

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (16,000) in cell F8 of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period) record the CO concentration from the ENVIDAS software 5 minute average in cell L8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The CO 10,000 ppm primary SRM should already be attached to the Environics 6103 (section 7.2 above), and the regulator should have already been purged (section 7.2). Set the timer for 15 minutes.

7.4.6 During the waiting time, write the diluent MFC settings (16,000) in cell F9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the CO concentration from the ENVIDAS software 5 minute average in cell L9, the Assay Worksheet. Record the Environics MFC settings and analyzer output in the logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 10 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary CO SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve a CO reading between 40-45 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 15 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (16,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the CO concentration from the ENVIDAS software 5 minute average in cell L10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows and CO analyzer readings should be entered in ranges F11..F14, and L11..L14, respectively for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range F20..F26, and analyzer results will be placed in cell range L20..L26.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range F32..F38, and analyzer results are reported in cell range L32..L48.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed Concentrations and Finalization of Assay Worksheet.

Note: This portion of the SOP will calculate the final concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

7.7.1 Scroll to cell R42 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.2 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.3 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → paste special → values → OK.

7.7.4 For challenge standard #1: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.5 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S70 → right click → paste special → values → OK.

7.7.6 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U94 → right click → paste special → values → OK.

7.7.7 For challenge standard #2: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.8 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V70 → right click → paste special → values → OK.

7.7.9 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X94 → right click → paste special → values → OK.

7.7.10 For challenge standard #3: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.11 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y70 → right click → paste special → values → OK.

7.7.12 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA94 → right click → paste special → values → OK.

7.7.13 For challenge standard #4: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.14 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB70 → right click → paste special → values → OK.

7.7.15 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD94 → right click → paste special → values → OK

7.7.16 For challenge standard #5: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.17 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → right click → copy. → go to the Assay Worksheet, highlight Cell AE70 → right click → paste special → values → OK.

7.7.18 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG94 → right click → paste special → values → OK

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-CO workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step	These are the various analytical steps taken to conduct this assay.
QA Requirement	Quality Assurance requirements are derived from the EPA Protocol
Result	These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.
Status	A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a “warning” level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-CO workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

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APPENDIX B:

WORKING INSTRUCTIONS

FOR

SULFUR DIOXIDE ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 2

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US EPA Region 2
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Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-SO2 v3.1.xls.** When using and/or archiving the PGVP-CO Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_S_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 -XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for SO2 data.

2.0 Assay Information Worksheet

The PGVP-SO2 Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: Flow calibrations are required within 2 weeks of any PGVP assay.

3.1 Calibration Procedure

The Environics 6103 calibration procedure is detailed in the Working Instructions for Carbon Monoxide Assays, and is not reproduced here. Current Environics 6103 flow calibration data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-SO2) in order to use the current calibration. The procedure for copying this data is as follows:

3.1.1 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet, highlight cell range B3..K28.

3.1.2 Select edit from the menu bar → clear→ all.

3.1.3 Go to the PGVP-CO workbook, Calibrator Flow Cal worksheet, → highlight cell range B1..K26 → right click → copy.

3.1.4 Select the PGVP-SO2 workbook, Calibrator Flow Cal worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

3.1.5 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet, delete all cells with data from row N50 and below.

3.1.6 Select the PGVP-CO workbook, Calibrator Flow Cal worksheet, highlight all cells with data commencing with cell N48 and below → right click →copy

3.1.7 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet → highlight cell N50 → right click → paste.

3.1.8 Close the PGVP-CO workbook that was used.

3.2 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and

intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 43i SO2 Analyzer Calibration Procedure & Analyzer Cal Worksheet

Note: The SO2 analyzer is set to a range of 0.500 ppm SO2.

Note: The SO2 analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: Initial upscale points require 60 minutes for SO2 equilibration. Later points require a 20 minute equilibration time

Note: The procedure for setting flow rates for the Environics 6103 is described in the Working Instructions for Carbon Monoxide Assays, Section 3.2, will not be repeated here.

4.1 Required Materials

a. Thermo 43i ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 100 ppm SO2 SRM and CGA 660 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-CO workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to SO2 Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn the on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the ½" output line from the Environics 6103 to the glass SO2 manifold. The SO2 analyzers are by default plumbed to the glass manifold via ¼" Teflon lines. The exhaust of the manifold is vented via a ½" line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the SO2 manifold. Let the SO2 analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 43i SO2 analyzer(s).

4.2.6 Install the CGA 660 regulator on the 100 ppm SO2 SRM cylinder. The cylinder should be charged overnight according to the following procedure.

g. Turn the delivery valve of the pressure regulator to the closed position.

h. Turn the cylinder valve of the SO2 SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

i. Set the pressure regulator delivery pressure for 30 psi.

j. Close the cylinder valve. The pressure regulator will remain under pressure.

k. Check to verify that the SRM cylinder valve is closed.

l. Let cylinder and regulator equilibrate overnight.

4.2.7 Purge the SO2 SRM regulator according to the following procedure:

a. Attach a ¼" delivery line to the pressure regulator connected to the SO2 SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.2.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the SO2 SRM to Port 2 of the Environics 6103.

4.2.9 Open the SO2 SRM cylinder valve and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Thermo 43i SO2 Analyzer Zero and Span

4.4.1 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 43i 20 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button (it is the 2^{nd} button down, on the left hand side of the analyzer and it has a page icon printed on it), and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER** (the enter button has a return icon printed on it and it is centered between the 4 directional arrow buttons used to move the cursor)**.** Record the **SO2 BKG** and **SO2 COEF** displayed on the Thermo 43i LCD in the laboratory logbook under the heading <u>Thermo 43i Pre Calibration Background & SO2 Coefficient Readings</u>. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 43i analyzer, and designated by a right pointing solid triangle icon).

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** A new screen will appear on the LCD with the cursor pointing to **CAL SO2 BACKGROUND**. Press **ENTER.** The Thermo 43i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET SO2 TO ZERO.** Press **ENTER.** After setting the zero, push the **RUN** button on the Thermo 43i front panel.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 16.0 L/min.

4.4.6 Allow the Thermo 43i to sample the Environics 6103 output for 60 minutes.

4.4.7 During this waiting period, open the Excel PGVP-SO2 Workbook that will be used for this batch of SO2 assays. The file naming conventions have been outlined in Section 1.0. The Assay Information worksheet should have already been filled out as per steps 2.0.

4.4.8 Go to the Analyzer Cal worksheet and enter 16000 in cell B13, the High MFC Device Setting. Cell F13 will display the delivered SO2 concentration at the current conditions (Environics 6103 set for 16.0 L/min diluent and 78.0 cc/min pollutant gas using the 100 ppm SO2 SRM).

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4.4.9 After the 60 minute waiting period and a steady data trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 43i display will show a new window with the cursor defaulting to the **CAL SO2 BACKGROUND** line. Using the front panel arrow keys, place the cursor in front of the **CAL SO2 COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.10 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered SO2 concentration specified in cell F13 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **RUN** button to get to the main screen of the Thermo 43i.

4.4.11 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.12 During the waiting period for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel, align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **SO2 BKG** and **SO2 COEF** displayed on the Thermo 43i front panel in the laboratory logbook under the heading Thermo 43i Post Calibration Background & SO2 Coefficient Readings. After taking the readings, push the **RUN** button to return to the Thermo 43i main screen.

4.4.13 After a steady trace is observed, record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading Post Calibration Zero.

4.5 Thermo 43i Calibration for the SO2 Assay Using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the Analyzer Cal worksheet from the Assay Info and Calibrator Flow Cal worksheets.

4.5.1 In the Analyzer Cal worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 20 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G13 (analyzer response) of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G14 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 20 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G15 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 20 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G16 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 20 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G17 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO_2 concentration from the ENVIDAS software in cell G18 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

4.6.1 In the Analyzer Cal worksheet collect the delivered SO_2 concentration and analyzer response: highlight cells F13..G18 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the calibration data for the SO_2 analyzer into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F13 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I13 → right click → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F14..F17 (one cell at a time), recording the results in cells I14..I17, respectively.

4.6.7 The analyzer estimate of uncertainty must be less than 1% for the Thermo 43i to be considered well characterized at that concentration, and thus allowing the analyzer to be used for SO_2 cylinder assays.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires assay of 2 SRMs of the same compound with different concentrations

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

5.1 Dilution Check Procedure

The Environics 6103 dilution check procedure is detailed in the Working Instructions for Carbon Monoxide Assays, Section 5.0, and is not reproduced here. Current Environics 6103 dilution check data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-SO2) in order to use the current calibration. The procedure for copying this data is as follows:

5.1.1 In the PGVP-SO2 workbook, Calibrator Dilution Check worksheet, highlight cell range B3..K35.

5.1.2 Select edit from the menu bar → clear→ all.

5.1.3 Go to the PGVP-CO workbook, Calibrator Dilution Check worksheet, → highlight cell range B2..K34 → right click → copy.

5.1.4 Select the PGVP-SO2 workbook, Calibrator Dilution Check worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

5.1.5 Close the PGVP-CO workbook that was used.

6.0 Day of Assay Zero, Span, and Precision Procedure and Day of Assay Zero & Span Worksheet

Note: Standard Procedure in Region 2 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-SO2 workbook for the current assay and open the Day of Assay Zero and Span worksheet.

Note: All non shaded cells have their values automatically entered into the Day of Assay Zero and Span worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 43i output data stream.

6.2.3 Equilibrate the regulator on the Primary SO2 SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 43i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary SO2 SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the sulfur dioxide glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 16,000 in the High MFC Device Setting column in cells D17..D22.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J17 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 60 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J18 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J19 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J20 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J21 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J22 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Assay Zero and Span Worksheet Finalization and Evaluation

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-SO2 Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

6.3.1 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J17, J19, and J21 → right click → copy.

6.3.2 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.3 Select the Day of Assay Zero and Span worksheet, collect the predicted SO2 response: press escape → left click on cells H18 → control-left click on H20, and H22 → right click → copy.

6.3.4 Select cell E233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.5 Select the Day of Assay Zero and Span worksheet, collect the analyzer SO2 concentration: press Escape → left click on cell J18 → control-left click on J20, and J22 → right click → copy.

6.3.6 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.3.8 Select the Day of Assay Zero and Span worksheet → select cell D26 → right click → paste special → values → OK.

6.3.9 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D28 and D30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.10 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F28 and F30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.11 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 SO2 Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary SO2 SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-SO2 workbook for the current assay and open the Assay Worksheet.

Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 43i output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 43i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary SO2 SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 the sulfur dioxide glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 43i SO2 analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-0.500 ppm. With challenge standard cylinder concentrations of 25 – 100 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart					
Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
SO2	100	100	16.0	70	0.433
	50	100	8.0	70	0.432
	25	100	4.0	70	0.430

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (16,000) in cell F8 of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period) record the SO2 concentration from the ENVIDAS software 5 minute average in cell L8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The SO2 100 ppm primary SRM should already be attached to the Environics 6103 (section 7.2 above), and the regulator should have already been purged (section

7.2). Set the timer for 30 minutes (initial equilibration for SO2 was done in Section 6.0, Day of Assay Zero and Span).

7.4.6 During the waiting time, write the diluent MFC settings (16,000) in cell F9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the SO2 concentration from the ENVIDAS software 5 minute average in cell L9 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 10 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary SO2 SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve an SO2 reading between 0.400-0.450 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 20 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (16,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the SO2 concentration from the ENVIDAS software 5 minute average in cell L10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder

regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows and SO2 analyzer readings should be entered in ranges F11..F14, and L11..L14, respectively for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range F20..F26, and analyzer results will be placed in cell range L20..L26.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range F32..F38, and analyzer results are reported in cell range L32..L48.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed Concentrations and Finalization of Assay Worksheet.

Note: This portion of the SOP will calculate the final concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it

into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

7.7.1 Scroll to cell R42 in the Assay Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.2 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.3 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.7.4 For challenge standard #1: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.5 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S70 → right click → paste special → values → OK.

7.7.6 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U94 → right click → paste special → values → OK.

7.7.7 For challenge standard #2: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.8 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V70 → right click → paste special → values → OK.

7.7.9 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X94 → right click → paste special → values → OK.

7.7.10 For challenge standard #3: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.11 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y70 → right click → paste special → values → OK.

7.7.12 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA94 → right click → paste special → values → OK.

7.7.13 For challenge standard #4: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.14 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB70 → right click → paste special → values → OK.

7.7.15 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD94 → right click → paste special → values → OK

7.7.16 For challenge standard #5: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.17 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE70 → right click → paste special → values → OK.

7.7.18 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG94 → right click → paste special → values → OK

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-SO2 workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step These are the various analytical steps taken to conduct this assay.

QA Requirement Quality Assurance requirements are derived from the EPA Protocol

Result These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.

Status A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a "warning" level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-SO2 workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

APPENDIX C:

WORKING INSTRUCTIONS

FOR

OXIDES OF NITROGEN ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 2

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Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-NOx v3.1.xls.** When using and/or archiving the PGVP-NOx Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_N_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 –XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for NOx data.

2.0 Assay Information Worksheet

The PGVP-NOx Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: The Environics 6103 must be calibrated within 2 weeks of any assay.

3.1 Calibration Procedure

The Environics 6103 calibration procedure is detailed in the Working Instructions for Carbon Monoxide Assays, and is not reproduced here. Current Environics 6103 flow calibration data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-NO/NOx) in order to use the current calibration. The procedure for copying this data is as follows:

3.1.1 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet, highlight cell range B3..K28.

3.1.2 Select edit from the menu bar → clear→ all.

3.1.3 Go to the PGVP-CO workbook, Calibrator Flow Cal worksheet, → highlight cell range B1..K26 → right click → copy.

3.1.4 Select the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

3.1.5 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet, delete all cells with data from row N50 and below.

3.1.6 Select the PGVP-CO workbook, Calibrator Flow Cal worksheet, highlight all cells with data commencing with cell N48 and below → right click →copy

3.1.7 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet → highlight cell N50 → right click → paste.

3.1.8 Close the PGVP-CO workbook that was used.

3.2 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and

intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 42i NO/NOx Calibration Procedure & Analyzer Cal Worksheet

Note: The analyzer is set to a range of 0.500 ppm NO/NOx.

Note: The NO/NOx analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: The NO/NOx Procedure measures NO *and* NOx to account for NO impurities. Therefore, there are extra fields for NO and NOx data in the Assay Info, Analyzer Cal, Day of Assay Zero and Span, Assay Worksheet, QA, and Certificate worksheets in the PGVP-NOX workbook.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: Initial upscale points require 40 minutes for NO/NOx equilibration. Later points require a 20 minute equilibration time

Note: The procedure for setting flow rates for the Environics 6103 is described in the Working Instructions for Carbon Monoxide Assays, Section 3.2, will not be repeated here.

4.1 Required Materials

a. Thermo 42iC ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 100 ppm NO/NOx SRM and CGA 660 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-NOx workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to NO/NOx Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn the on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the ½" output line from the Environics 6103 to the glass NO/NOx manifold. The NO/NOx analyzers are by default plumbed to the glass manifold via ¼" Teflon lines. The exhaust of the manifold is vented via a ½" line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the NO/NOx manifold. Let the NO/NOx analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 42i NO/NOx analyzer(s).

4.2.6 Install the CGA 660 stainless steel regulator on the 100 ppm NO/NOx SRM cylinder. The cylinder should be charged overnight according to the following procedure.

a. Turn the delivery valve of the pressure regulator to the closed position.

b. Turn the cylinder valve of the NO/NOx SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

c. Set the pressure regulator delivery pressure for 30 psi.

d. Close the cylinder valve. The pressure regulator will remain under pressure.

e. Check to verify that the SRM cylinder valve is closed.

4.2.7 Purge the NO/NOx SRM regulator according to the following procedure:

a. Attach a ¼" delivery line to the pressure regulator connected to the NO/NOx SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.1.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the NO/NOx SRM to Port 2 of the Environics 6103.

4.2.9 Open the NO/NOx SRM cylinder valve and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Calibration of the Thermo 42i NO/NOx Analyzer

4.4.1 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 42i 20 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button (it is the 2^{nd} button down, on the left hand side of the analyzer and it has a page icon printed on it), and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER** (the enter button has a return icon printed on it and it is centered between the 4 directional arrow buttons used to move the cursor)**.** Record the **NO BKG, NOx BKG, NO COEF,** and **NOX COEF** displayed on the Thermo 42i LCD in the laboratory logbook under the heading Thermo 42i Pre Calibration Background & NO/NOx Coefficient Readings. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 42i analyzer, and designated by a right pointing solid triangle icon).

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** A new screen will appear on the LCD with the cursor pointing to **CAL NO BACKGROUND**. Press **ENTER.** The Thermo 42i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET NO TO ZERO.** Press **ENTER.** After setting the NO zero, push the **MENU** button on the Thermo 42i front panel. This will bring you back to the previous screen. Push the down arrow on the front panel to bring cursor in front of the **CAL NOX BACKGROUND** line, and push **ENTER**. The Thermo 42i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET NOX TO ZERO.** Press **ENTER**. After setting the NOx zero, push the **RUN** button to resume at the main display screen.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 16.0 L/min.

4.4.6 Allow the Thermo 42i to sample the Environics 6103 output for 40 minutes.

4.4.7 During this waiting period, open the Excel <u>PGVP-NO/NOx Workbook</u> that will be used for this batch of NO/NOx assays. The <u>Assay Information</u> worksheet should have already been filled out as outlined in Section 2.0 above.

4.4.8 Go to the <u>Analyzer Cal</u> worksheet and enter 16000 for the High MFC Device setting in cells B14 (NO portion of analyzer calibration) and B23 (NOX portion of analyzer calibration). The delivered concentration will be displayed in cell F14 (for NO) and Cell F23 (for NOx), for the current conditions (Environics 6103 set for 16.0 L/min diluent and 78.0 cc/min pollutant gas using the 100 ppm NO/NOx SRM).

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4.4.9 After the 40 minute waiting period and a steady data trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 42i display will show a new window with the cursor defaulting to the **CAL NO BACKGROUND** line. Using the front panel arrow keys, place the cursor in front of the **CAL NO COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.10 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered NO/NOx concentration specified in cell F14 of the <u>Analyzer Cal</u> worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **MENU** button to get to the previous screen on the Thermo 42i.

4.4.11 Using the front panel arrow keys, place the cursor in front of the **CAL NOX COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer NOx reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.12 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered NO/NOx concentration specified in cell F23 of the <u>Analyzer Cal</u> worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **MENU** button to get to the main analyzer screen on the Thermo 42i.

4.4.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.14 During the waiting time for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **NO BKG, NOx BKG, NO COEF,** and **NOX COEF** displayed on the Thermo 42i LCD in the laboratory logbook under the heading <u>Thermo 42i Post Calibration Background & NO/NOx Coefficient Readings</u>. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 42i analyzer, and designated by a right pointing solid triangle icon).

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4.4.15 After a steady trace is observed , record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading <u>Post Calibration Zero</u>.

4.5 Thermo 42i Calibration for the NO/NOx Assay using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the <u>Analyzer Cal</u> worksheet from the <u>Assay Info</u> and <u>Calibrator Flow Cal</u> worksheets.

4.5.1 In the <u>Analyzer Cal</u> worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 20 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G14 (analyzer response), and the NOX concentration in cell G23 of the <u>Analyzer Cal</u> worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G15, and the NOX concentration in cell G24 of the <u>Analyzer Cal</u> worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 20 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G16, and the NOX concentration in cell G25 of the <u>Analyzer Cal</u> worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 20 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G17, and the NOX concentration in cell G26 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 20 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G18, and the NOX concentration in cell G27 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G19, and the NOX concentration in cell G28 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

Note: The analyzer uncertainty estimate must be calculated separately for the NO and NOx components.

4.6.1 In the Analyzer Cal worksheet, collect the delivered NO concentration and analyzer response: highlight cells F14..G19 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer calibration data for NO into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F14 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I14 → right click → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F15..F18 (one cell at a time), recording the results in cells I15..I18, respectively.

4.6.7 In the Analyzer Cal worksheet, collect the delivered NOx concentration and analyzer response: highlight cells F23..G28 → right click → copy.

4.6.8 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer calibration data for NOx into this worksheet.

4.6.9 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.10 Select cell F23 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.11 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I23 → right click → paste special → values → OK.

4.6.12 Repeat steps 4.6.10 and 4.6.11 for each cell in the range F24..F27 (one cell at a time), recording the results in cells I24..I27, respectively.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires assay of 2 SRMs of the same compound with different concentrations

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

5.1 Dilution Check Procedure

The Environics 6103 dilution check procedure is detailed in the Working Instructions for Carbon Monoxide Assays, Section 5.0, and is not reproduced here. Current Environics 6103 dilution check data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-NO/NOx) in order to use the current calibration. The procedure for copying this data is as follows:

5.1.1 In the PGVP-NO/NOx workbook, Calibrator Dilution Check worksheet, highlight cell range B3..K35.

5.1.2 Select edit from the menu bar → clear→ all.

5.1.3 Go to the PGVP-CO workbook, Calibrator Dilution Check worksheet, → highlight cell range B2..K34 → right click → copy.

5.1.4 Select the PGVP-NO/NOx workbook, Calibrator Dilution Check worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

5.1.5 Close the PGVP-CO workbook that was used.

6.0 Day of Assay Zero, Span, and Precision Procedure and Day of Assay Zero & Span Worksheet

Note: Standard Procedure in Region 2 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-NOx workbook for the current assay and open the Day of Assay Zero and Span worksheet.

Note: All non shaded cells have their values automatically entered into the Day of Assay Zero and Span worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 42i output data stream.

6.2.3 Equilibrate the regulator on the Primary NO/NOx SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 42i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary NO/NOx SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the NO/NOx glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 16,000 in the High MFC Device Setting column in cells D18..D23 and D41..D46.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J18 for NO and J41 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 40 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J19 for NO and J42 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J20 for NO and J43 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J21 for NO and J44 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J22 for NO and J45 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J23 for NO and J46 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Assay Zero and Span Worksheet Finalization and Evaluation for NO

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-NOx Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

Note: This assay is for both NO and NOx. These two pollutants have different calibrations. In order to determine the instrument drift via the analysis of day of assay zero and span, the appropriate analyzer calibration data must first be loaded into the Measurement Data worksheet. This is done, for NO, in steps 6.3.1 - 6.3.2 below.

6.3.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F14..G19 → right click → copy. This is done to collect the NO calibration data originally obtained in Section 4.0.

6.3.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer NO calibration data into this worksheet.

6.3.3 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J18, J20, and J22 → right click → copy.

6.3.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.5 Select the Day of Assay Zero and Span worksheet, collect the predicted NO concentration: press escape → left click on cell H19 → control-left click on H21, and H23 → right click → copy.

6.3.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NO response: press Escape → left click on cell J19 → control-left click on J21, and J23 → right click → copy.

6.3.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.9 In the Measurement Data worksheet, select cell range D249..G253 → copy.

6.3.10 Select the Day of Assay Zero and Span worksheet → select cell D27 → right click → paste special → values → OK.

6.3.11 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D29 and D31, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.3.12 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F29 and F31, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4 Day of Assay Zero and Span Worksheet Finalization and Evaluation for NOx

Note: This assay is for both NO and NOx. These two pollutants have different calibrations. In order to determine the instrument drift via the analysis of day of assay zero and span, the appropriate analyzer calibration data must first be loaded into the Measurement Data worksheet. This is done, for NOx, in steps 6.4.1 - 6.4.2 below.

6.4.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F23..G28 → right click → copy. This is done to collect the NOx calibration data originally obtained in Section 4.0.

6.4.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer NOx calibration data into this worksheet.

6.4.3 In the Day of Assay Zero and Span worksheet collect the response to zero gas: control-left click on cells J41, J43, and J45 → right click → copy.

6.4.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.4.5 Select the Day of Assay Zero and Span worksheet collect the predicted NOx concentration: press escape → left click on cell H42 → control-left click on H44, and H46 → right click → copy.

6.4.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.4.7 Select the Day of Assay Zero and Span worksheet collect the analyzer NOx response: press Escape → left click on cell J42 → control-left click on J44, and J46 → right click → copy.

6.4.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.4.9 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.4.10 Select the Day of Assay Zero and Span worksheet → select cell D50 → right click → paste special → values → OK.

6.4.11 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D52 and D54, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4.12 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F52 and F54, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4.13 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 and 6.4.9 and 6.4.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 NO/NOx Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary NO/NOx SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-NOx workbook for the current assay and open the Assay Worksheet.

> **Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.**

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 42i output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 42i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary NO/NOx SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 to the NO/NOx glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 42i NO/NOx analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-0.500 ppm (0-500 ppb). With challenge standard cylinder concentrations of 25 – 100 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart

Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
NO or NOx	100	100	16.0	70	0.433
	50	100	8.0	70	0.432
	25	100	4.0	70	0.430

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (16,000) in cell G8 and of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period) record the NO concentration from the ENVIDAS software 5 minute average in cell M8, and the NOx concentration in cell N8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The NO/NOx 100 ppm primary SRM should already be attached to the

Environics 6103 (section 7.2 above), and the regulator should have already been purged (section 7.2). Set the timer for 40 minutes.

7.4.6 During the waiting time, write the diluent MFC settings (16,000) in cell G9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the NO/NOx concentration from the ENVIDAS software 5 minute average in cell M9, and the NOx concentration in cell N9 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 15 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary NO/NOx SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve a NO/NOx analyze reading between 0.400-0.450 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 15 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (16,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the NO/NOx concentration from the ENVIDAS software 5 minute average in cell M10, and the NOx concentration in cell N10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder

regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows NO, and NOx analyzer readings should be entered in ranges G11..G14, M11..M14, and N11..N14 \, respectively, for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range G20..G26, and analyzer NO and NOx results will be placed in cell range M20..M26 and N20..N26. respectively.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range G32..G38, and analyzer NO and NOx results are reported in cell range M32..M38 and N32..N38, respectively.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed NO Concentrations and Finalization of NO Portion of the Assay Worksheet.

Note: This portion of the SOP will calculate the final NO concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

Note: This assay includes both NO and NOx results. Section 7.7 pertains to the NO portion of the assay, and both the analyzer calibration data for NO, as well as the day of assay zero and span results must be re-entered into the Measurement Data worksheet. In Section 7.8, the same process will be applied to NOx results.

7.7.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F14..G19 → right click → copy. This is done to collect the NO calibration data originally obtained in Section 4.0.

7.7.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer NO calibration data into this worksheet.

7.7.3 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J18, J20, and J22 → right click → copy.

7.7.4 Select cell C233 in the Measurement Data worksheet, → right click → paste special → values → OK.

7.7.5 Select the Day of Assay Zero and Span worksheet, collect the predicted NO concentration: press escape → left click on cell H19 → control-left click on H21, and H23 → right click → copy.

7.7.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.7.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NO response: press Escape → left click on cells J19 → control-left click on J21, and J23 → right click → copy.

7.7.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.7.9 Scroll to cell R42 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.10 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.11 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.7.12 **For challenge standard #1**: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.13 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S75 → right click → paste special → values → OK.

7.7.14 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U99 → right click → paste special → values → OK.

7.7.15 **For challenge standard #2**: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.16 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V75 → right click → paste special → values → OK.

7.7.17 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X99 → right click → paste special → values → OK.

7.7.18 **For challenge standard #3**: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.19 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y75 → right click → paste special → values → OK.

7.7.20 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA99 → right click → paste special → values → OK.

7.7.21 For challenge standard #4: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.22 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB75 → right click → paste special → values → OK.

7.7.23 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD99 → right click → paste special → values → OK

7.7.24 For challenge standard #5: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.25 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE75 → right click → paste special → values → OK.

7.7.26 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG99 → right click → paste special → values → OK.

7.8 Determination of Assayed NOx Concentrations and Finalization of NOx Portion of the Assay Worksheet.

Note: This portion of the SOP will calculate the final NOx concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

Note: This assay includes both NO and NOx results. Section 7.8 pertains to the NOx portion of the assay, and both the analyzer calibration data for NOx, as well as the day of assay zero and span results must be re-entered into the Measurement Data worksheet.

7.8.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F23..G28 → right click → copy. This is done to collect the NOx calibration data originally obtained in Section 4.0.

7.8.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer NOx calibration data into this worksheet.

7.8.3 In the Day of Assay Zero and Span worksheet collect the response to zero gas: control-left click on cells J41, J43, and J45 → right click → copy.

7.8.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

7.8.5 Select the Day of Assay Zero and Span worksheet collect the predicted NOx concentration: press escape → left click on cells H42 → control-left click on H44, and H46 → right click → copy.

7.8.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.8.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NOx response: press Escape → left click on cells J42 → control-left click on J44, and J46 → right click → copy.

7.8.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.8.9 Scroll to cell R102 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.8.10 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S108..T110 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.8.11 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U108..V110 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.8.12 **For challenge standard #1**: In the Assay Worksheet, highlight cells W108..W110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.13 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S135 → right click → paste special → values → OK.

7.8.14 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U159 → right click → paste special → values → OK.

7.8.15 For challenge standard #2: In the Assay Worksheet, highlight cells X108..X110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.16 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V135 → right click → paste special → values → OK.

7.8.17 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X159 → right click → paste special → values → OK.

7.8.18 For challenge standard #3: In the Assay Worksheet, highlight cells Y108..Y110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.19 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y135 → right click → paste special → values → OK.

7.8.20 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA159 → right click → paste special → values → OK.

7.8.21 For challenge standard #4: In the Assay Worksheet, highlight cells Z108..Z110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.22 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB135 → right click → paste special → values → OK.

7.8.23 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD159 → right click → paste special → values → OK

7.8.24 For challenge standard #5: In the Assay Worksheet, highlight cells AA108..AA110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.25 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE135 → right click → paste special → values → OK.

7.8.26 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG159 → right click → paste special → values → OK.

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-NOx workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step	These are the various analytical steps taken to conduct this assay.
QA Requirement	Quality Assurance requirements are derived from the EPA Protocol
Result	These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.
Status	A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a "warning" level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-NOx workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by the comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

APPENDIX D:

SCREEN SHOTS

FROM THE

PGVP-CO WORKBOOK

PGVP Carbon Monoxide Assay Information

EPA Region 2

Laboratory & Location:	EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ	Date of PGVP Assay:	11-Feb-10
Verification Conducted By:	Avi Teitz/Mustafa Mustafa	Laboratory Manager:	Avi Teitz/Mustafa Mustafa

SRM Standards for Carbon Monoxide Assays

Type of Standard	Manufacturer	SRM #	Cylinder Serial #	Concentration (ppm)	Cylinder Pressure During Assay	Expiration Date	Notes
Primary Std.	Scott	SRM 2639a	ALM1234567	9982	1200	31-Mar-11	
Check Std.	Praxair	SRM 2638a	FF1234567	5000	900	31-Mar-11	

Laboratory Flow Standards

Manufacturer	Model #	Serial #	Certification Date	Range	Notes
BIOS	ML-800 Cell 44	104396	5-May-10	0.5 - 30L/min	High Flow Cell
BIOS	ML-800 Cell 10	106328	5-May-10	5-300 cc/min	Low Flow Cell
BIOS	ML-800 Base	105428	5-May-10	N/A	Base unit w/ Temp & Pressure

Gas Dilution Calibrator Information

Manufacturer	Model #	Serial #	Calibrator Calibration Date	Notes
Environics	6103	4501	9-Feb-10	

CO Analyzer Information

Date of Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Slope	Intercept	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	1.00377	0.0663	

Carbon Monoxide Challenge Standards Under Test

Vendor	Cylinder Serial Number	Vendor Certified Concentration (ppm)	Balance Gas	Vendor Expiration Date	Date Received	Cylinder Pressure Received (psig)	Cylinder Pressure After Assay (psig)	Notes
Scott-Marrin	B12345678	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1800	1780	
Scott	C98765432	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1900	1880	
Praxair	D12345678	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1850	1825	
BOC	E98765432	10000.00	Nitrogen	1-Jan-12	1-Dec-09	2000	1980	
Joe Blow	F12345678	2500.00	Nitrogen	1-Jan-12	1-Dec-09	1750	1725	

Calibrator Flow Calibration

Calibrator Information

Calibration Date	Manufacturer	Model #	Serial #	Notes
9-Feb-10	Environics	6103	4501	

Flow Standard Information

Manufacturer	Model #	Serial #	Annual Certification Date	Range	Notes
BIOS	ML-800 Cell 44	104396	5-May-10	0.5 - 30L/min	High Flow Cell
BIOS	ML-800 Cell 10	106328	5-May-10	5-300 cc/min	Low Flow Cell
BIOS	ML-800 Base	105428	5-May-10	N/A	Base unit w/ Temp & Pressure

Flow Calibration

February 9, 2010

Zero Gas Mass Flow Controller					Pollutant Gas Mass Flow Controller				
MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction	MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction
16000	16010	15918	15913	-0.03%	78	78.10	77.16	77.11	-0.07%
12000	12008	11923	11926	0.02%	70	70.00	69.17	69.19	0.03%
8000	8006	7931	7939	0.11%	60	59.90	59.23	59.29	0.10%
6000	6019	5946	5946	-0.01%	50	49.90	49.38	49.39	0.02%
4000	4008	3958	3952	-0.15%	40	40.10	39.54	39.49	-0.10%
Slope		0.996744085	Slope of Calibrated MFC	0.999998504	Slope		0.989796423	Slope of Calibrated MFC	0.999990601
Intercept		-34.85673835	Intercept of Calibrated MFC	0.013668974	Intercept		-0.097130622	Intercept of Calibrated MFC	0.000553546

Select-a-Cal

Calibration Flow Selection Tool

February 9, 2010

Pollutant	Nominal Pollutant Concentration (ppm)	Zero MFC Setting (cc/min)	Zero MFC Predicted Flow (cc/min)	Pollutant MFC Setting (cc/min)	Pollutant MFC Predicted Flow (cc/min)	Predicted Concentration Delivered (ppm)
CO	10000	16000	15913.0	78	77.11	48.222
				70	69.19	43.291
				60	59.29	37.121
				50	49.39	30.943
				40	39.49	24.758

CO Analyzer Calibration

CO Analyzer Information

Date of Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

Delivered CO Concentration and Analyzer Response

High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Delivered CO Concentration (ppm)	Analyzer Response (ppm)	% Difference	Estimate of Uncertainty @ Each Calbration Point (Step 4 of prot97aa.xls spreadsheet)	Analyzer Calibration Curve Parameters	
16000	15913.0	78	77.11	**48.14**	**48.40**	0.55	**0.60%**	slope	1.003775
		70	69.19	**43.21**	**43.50**	0.66	**0.62%**		
		60	59.29	**37.06**	**37.20**	0.39	**0.67%**		
		50	49.39	**30.89**	**31.10**	0.69	**0.79%**	intercept	0.0662707
		40	39.49	**24.71**	**24.80**	0.35	**1.00%**		
		0	0.00	**0.00**	**0.10**				

Dilution Calibrator Leak Check

Calibrator Information

Date of Dilution Check	Calibration Date	Manufacturer	Model #	Serial #	Notes
11-Feb-10	9-Feb-10	Environics	6103	4501	

CO Analyzer Information

Date of Analyzer Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO Primary SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

CO Check SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2638a	CO	Praxair	5000.0	FF1234567	900	31-Mar-11

Dilution Check w/ CO Analyzer

Gas Type	Cylinder Concentrations	High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Predicted Calibrator Delivered Concentration	Predicted Analyzer Response	Actual Analyzer Response	Percent Difference
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	43.2	-0.56
Zero Gas	0	16000	15913.0	0	0.00	**0.00**	**0.07**	0.1	
Check SRM	5000	8000	7939.1	70	69.19	**43.20**	**43.43**	43.3	-0.29
Zero Gas	0	8000	7939.1	0	0.00	**0.00**	**0.07**	0.0	
Check SRM	5000	8000	7939.1	70	69.19	**43.20**	**43.43**	43.4	-0.06
Zero Gas	0	8000	7939.1	0	0.00	**0.00**	**0.07**	0.1	
Check SRM	5000	8000	7939.1	70	69.19	**43.20**	**43.43**	43.3	-0.29
Zero Gas	0	8000	7939.1	0	0.00	**0.00**	**0.07**	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	43.2	-0.56
					Average Check SRM Response =			**43.3**	

Relative % Difference **-0.217%**

Relative % Difference must be less than 1% to qualify the calibrator for use in assays.

Day of Assay Carbon Monoxide Zero and Span Check

CO Analyzer Information

Date of Analyzer Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO Primary SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

CO Analyzer Zero/Span Results

Gas Type	Cylinder Concentrations	High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Predicted Calibrator Delivered Concentration	Predicted Analyzer Response	Actual Analyzer Response	Percent Difference
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.9	-1.25
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.0	
Primary SRM SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.8	-1.48
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.9	-1.25

Average Zero Gas Response =	**0.1**
Average Primary SRM Response =	**42.9**

	Zero Gas Results	Span Gas Results
Std. Error = s/sqrt(n) =	0.03	0.03
Rrs/100 =	0.42866667	0.42866667
	Std. Error is okay.	Std. Error is okay.
Relative Difference (RD)=	-0.14%	-0.77%
	RD is okay.	RD is okay.

EPA Region 2 CO Assay

Assay Date: 11-Feb-10 **Assay Site:** EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ **Assay Conducted By:** Avi Teitz/Mustafa Mustafa

Test Set 1

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0	0.07	0.051	n/a
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	42.260	-2.2%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.500	0.7%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.700	3.5%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.600	-1.4%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	41.800	-3.4%
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.000	0.0%

Test Set 2

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	43.380	0.4%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.700	-1.2%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.800	3.7%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.400	0.5%
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0	0.07	0.080	n/a
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.130	0.3%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	41.900	-3.2%

Test Set 3

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.200	0.4%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	42.000	-3.0%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.800	-0.9%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.600	3.2%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.700	1.2%
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	42.260	-2.2%
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0.00	0.07	0.900	n/a

QA Requirements Summary

	QA Requirement	Result	Status
SRM Gas Standards	Primary SRM Cylinder Expiration Date	31-Mar-11	Primary SRM Gas Standard OK
	Primary SRM Cylinder Pressure >150 psi	1200	Primary SRM cylinder pressure is OK
	SRM Dilution Check Cylinder Expiration Date	31-Mar-11	Dilution Check SRM Gas Standard OK
	Dilution Check SRM Cylinder Pressure >150 psi	900	Dilution check SRM cylinder pressure is OK
Laboratory Flow Standard	High Flow Standard Expiration Date	5-May-10	Standard OK
	Low Flow Standard Expiration Date	5-May-10	Standard OK
	Flow Standard Base Unit Expiration Date	5-May-10	Standard OK
Calibrator (mass flow controllers)	Calibrator Flow Calibration within 2 weeks of assay	9-Feb-10	Calibrator flow calibration within 2 weeks of assay
	Calibrated High Flow MFC Slope Range = 0.99 - 1.01	0.9999985	High MFC OK
	Calibrated Low Flow MFC Slope Range = 0.99 - 1.01	0.9999906	Low MFC OK
Carbon Monoxide Gas Analyzer	Analyzer Calibration within 2 week of assay	9-Feb-10	Analyzer calibration within 2 weeks of assay
	Estimate of Uncetainty < 1% at point #1 (>80% URL)	0.60%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #2	0.62%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #3	0.67%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #4	0.79%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #5 (~50% URL)	1.00%	Assay is invalid at this concentration
	Analyzer slope is within 0.98-1.02	1.0038	Analyzer Slope is acceptable
Dilution Check	Dilution Check Date within 2 weeks of assay	11-Feb-10	Dilution check within 2 weeks of assay
	Dilution Check Relative % Difference < 1%	-0.217%	Dilution Check RSD is OK
Day of Assay Zero/Span Check	Day of Assay Zero Check - Std. Error < 1%	Std. Error is okay.	Zero Gas Std. Error is OK
	Day of Assay Zero Check - Relative Difference < 5%	RD is okay.	Zero Gas RD is OK
	Day of Assay Span Check - Std. Error < 1%	Std. Error is okay.	Span Gas Std. Error is OK
	Day of Assay Span Check - Relative Difference <5%	RD is okay.	Span Gas RD is OK
Challenge Standard #1 Assay	Challenge Standard #1 Std. Error < 1%	The standard error is okay.	Challenge Standard #1 Std. Error is OK
	Challenge Standard #1 vendor certificate bias	2.17%	Challenge Std. #1 vendor certificate bias between 2-4%
Challenge Standard #2 Assay	Challenge Standard #2 Std. Error < 1%	The standard error is okay.	Challenge Standard #2 Std. Error is OK
	Challenge Standard #2 vendor certificate bias	4.93%	Challenge Std. #2 vendor certificate bias is 4% or greater
Challenge Standard #3 Assay	Challenge Standard #3 Std. Error < 1%	The standard error is okay.	Challenge Standard #3 Std. Error is OK
	Challenge Standard #3 vendor certificate bias	0.20%	Challenge Std. #3 vendor certificate bias < 2%
Challenge Standard #4 Assay	Challenge Standard #4 Std. Error < 1%	The standard error is okay.	Challenge Standard #4 Std. Error is OK
	Challenge Standard #4 vendor certificate bias	-1.91%	Challenge Std. #4 vendor certificate bias < 2%
Challenge Standard #5 Assay	Challenge Standard #5 Std. Error < 1%	The standard error is okay.	Challenge Standard #5 Std. Error is OK
	Challenge Standard #5 vendor certificate bias	1.60%	Challenge Std. #5 vendor certificate bias < 2%

Challenge Cylinder #3 Certificate

EPA Protocol Gas Verification Program

Date of Assay: **24-Mar-10**

Cylinder under Test:	**Scott-Marrin LL101544**
Pollutant Gas:	**Sulfur Dioxide**
Balance Gas:	**Nitrogen**
Cylinder Pressure After Assay:	**1780 psig**

Assayed SO2 Concentration =	**70.83**
Vendor Certified SO2 Concentration =	**71.20**
% bias =	**-0.52%**
95% uncertainty of analysis =	**0.29%**

Reference Gas:	**SRM 1694a CAL016709**
Expiration Date:	**11-Dec-15**
Analyst:	**Avi Teitz/Mustafa Mustafa**
Analytical Facility:	**EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ**

Standard Operating Procedures for the Verification of NO/NOx, SO2, and CO Concentrations in EPA Protocol Gas Mixtures

Avraham Teitz – EPA Region 2
Thien Bui – EPA Region 7

March 25, 2010

Approved:

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Avraham Teitz, US EPA Region 2

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Thien Bui, US EPA Region 7

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Michael Papp, OAQPS

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XXXXXXX, OAQPS

Page

2.0 Purpose

The purpose of this procedure is to verify the concentration of CO, SO2, NO, and NOx in gas standards purchased by State, Local and Tribal monitoring agencies that have been certified by the gas vendor as meeting the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121).

3.0 Scope

This document is an adaptation of the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) using the specific equipment, tools, and resources available to the Region 2 Ambient Monitoring Standards Laboratory. This document is designed for use by trained air monitoring personnel in order to assure consistent laboratory practices in the verification of CO, SO2, NO, NOx concentrations in cylinder standards designated by the gas vendor as meeting the EPA Protocol referenced above. Untrained users, familiar with good laboratory practices, may also find this a useful guide, although specific air monitoring knowledge is assumed by the authors.

4.0 SOP Availability

This SOP shall be available as a reference in the Ambient Air Monitoring Standards Laboratory work area during the course of all verification of EPA Protocol Gases by EPA Region 2, as well as the Monitoring and Assessments Branch Master File of Ambient Air Monitoring SOPs located in the G:\User\DESA\MAB\AWQAT\Ambient Air Monitoring\SOPs folder on the Regional Computer Server.

5.0 Revisions

This SOP shall be reviewed annually to ensure that the policies and procedures remain current and appropriate. The SOP will be modified whenever the calibration procedures are changed.

6.0 Inherently Governmental Functions

This method is to ensure compliance with 40CFR Part 58 Appendix A, Section 2.6 which requires gas vendors to participate in an EPA Protocol Gas Verification Program. As such this program is an inherently governmental function.

7.0 Definitions

SRM = Standard Reference Material, obtained from NIST
NIST = National Institute of Science and Technology

G2 Protocol = Portion of the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) pertaining to assay of gas with dilution of reference and candidate standards.

Protocol Gas = a compressed gas cylinder assayed by the vendor according to the EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121).

Analyzer = EPA reference and equivalent analyzers. In this particular SOP it refers to either a Thermo 48C or 48i (CO), Thermo 42i (NO/NOx), or Thermo 43i (SO2).

CO = Carbon Monoxide
SO2 = Sulfur Dioxide
NO = Nitrous Oxide
NO2 = nitrogen dioxide
NOx = Oxides of Nitrogen
Calibrator = A gas phase titration calibrator, such as a Environics 6103
Zero Air = diluent gas free of contaminants
Candidate cylinder = a protocol gas cylinder under test for assay.
MFC = Mass Flow controller, found in the calibrator
Laboratory Primary Flow Standard= BIOS ML-800 (Region 2), BIOS DC-DEFINER 220 (Region 7)
Primary Standard = An NIST SRM gas cylinder (NO/NOx, SO2, or CO)
Check Standard = A NIST SRM gas cylinder (NO/NOx, SO2, or CO) at a different concentration than the primary standard
URL = Upper Range Limit of an ambient air analyzer

8.0 Safety Warnings

This SOP requires the use of compressed gas cylinders under high pressure (150-2000 psig). Therefore, cylinder handling safety is of primary importance. Cylinders must be capped while moving and secured with appropriate restraints during use. Pressure regulators should be properly tightened before cylinder valves are opened. Make certain that the pressure regulator is adjusted so that equipment downstream will not be pressurized above anticipated values.

This procedure makes use of cylinder gases at the following concentrations; CO at 2500-10,000 ppm for diluted standards and 40-50 ppm for undiluted standards, and NO/NOx and SO2 at 25-100 ppm. Gases at delivery are at the following concentrations; CO at 25-50 ppm, and NO and SO2 at 250-500 ppb. Since excess gas at delivery is required, make sure that adequate ventilation and/or exhaust manifolds are present when using this procedure.

9.0 Procedural Cautions

The 1/8" tubing that is connected to the cylinder can easily crack if abused or twisted. This failure is not always easily seen, particularly when the break occurs at the fitting nut. Significant loss of SRM gas will result. If the cylinder valve is left open at the end of the day, even if the regulator outlet is shut, significant losses of SRM may occur in the ensuing days/weeks until it is used again. SRM gas is expensive and difficult to obtain. **Regularly check the cylinder pressure levels while the cylinder is in use, so that any leaks may be quickly repaired. Check and double check all cylinder valves at the end of the day to be certain that the SRM cylinder is closed**.

NO/NOx and SO2 analysis require an equilibrated regulator that has been pressurized overnight with gas. Failure to do so may result in long equilibration times and potentially inaccurate or variable results.

The SO2 assay requires a considerable amount of time (45 minutes – 1 hour) to reach equilibration during the first span point of the day, particularly if the gas handling system (cylinder/tubing/calibrator/analyzer/manifold) has not been used to generate upscale points in the previous 24 hours. Treat the equilibration times given in this procedure as minima, and observe them scrupulously, as the accuracy of the assay is dependent on it.

10.0 Summary of Method

The EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121) G2 methodology will be followed. As implemented, a mass flow controlled gas calibrator will be used to dilute either a NIST Standard Reference Material (SRM) or a State/Local provided EPA Protocol gas. The resulting diluted gas will be analyzed using an EPA reference or equivalent ambient air analyzer. Flow calibrations will be based on a BIOS DEFINER 220 primary flow standard.

11.0 Apparatus and Materials

NIST SRM 2637a CO @ 2,500 ppm
NIST SRM 2639a CO @ 10,000 ppm
NIST SRM 2638a CO @ 5,000 ppm
NIST SRM 1694a SO2 @ 100 ppm
NIST SRM 1693a SO2 @ 50 ppm
NIST SRM 1684a NO @ 100 ppm
NIST SRM 1683b NO @ 50 ppm
Thermo 48C (or 48i) CO analyzer
Thermo 43i SO2 analyzer
Thermo 42i NO/NOx analyzer
Environics 6103 gas phase titration calibrators
BIOS ML-800 (Region 2 Laboratory) or BIOS Definer (Region 7 Laboratory) Primary flow standard with 0-30 liter cell and 0-500 cc cell
Four stainless steel CGA 660 regulators for SO2/NOx analysis
Two brass CGA 350 regulators for CO analysis

House zero air gas supply sufficient for 20 L/minute
Envidas computer data acquisition system
50 feet of ¼" o.d. thick walled Teflon tubing
50 feet of 1/8" o.d. thick walled Teflon tubing
¼" and 1/8" Swagelok nuts and ferrules
Calculations spreadsheet from EPA Protocol (EPA-600/R-97/121), 9/1997 edition
Computer
Protocol Gas Verification Program Working Instructions for CO, SO2, and NO/NOx
Laboratory logbook

12.0 Preparation

All NIST SRMs and the DEFINER 220 must be within their certification dates. The analyzer, calibrator, and cylinder regulator must be equilibrated prior to commencement of this assay. Ideally, all equilibration should start the night before and include:

Powering up of the calibrator, zero air supply, and analyzer.

Supplying the analyzer with zero air at a sufficient flow volume such that excess air is drawn into the exhaust manifold. In our case the accepted volume is 3 liters/minute.

Pressurizing the regulator

Failure to equilibrate the regulator can result in lengthy equilibration times, on the order of 2 to 3 hours. Failure to adequately equilibrate the analyzer and calibrator can result in lengthy equilibration delays as well as erroneous results. Detailed information on these requirements and procedures may be found in the working instructions, which are presented in the Appendices.

13.0 Procedure

The procedure for assay is presented in exhaustive detail in the working instructions for CO, SO2, and NO/NOx in the Appendices. Presented below is an outline of the procedure:

13.1 Flow Calibration of Environics 6103 Calibrators

Environics 6103 calibrators, used for dilution of zero and reference/candidate standards, will have their mass flow controllers calibrated within 2 weeks of any assay utilizing a BIOS DEFINER 220 primary standard that has been certified by an NVLAP Laboratory.

13.2 Analyzer Calibration

CO, SO2, and NO/NOx ambient air analyzers will be calibrated from 50% to 90% of their upper range limit (URL). This is the most accurate range for these analyzers. Analyzers must be calibrated within 2 weeks of any assay.

13.3 Calibrator Dilution Check

The quarterly calibrator dilution check procedure are specified in detail, in the in the working instructions presented in the Appendices. The dilution check consists of: 1) multipoint calibration of the ambient air analyzer as stated in Section 13.2, utilizing a 5,000 ppm CO SRM, followed by 2) generation of 3 discrete points >80% of the instrument URL with the same calibrator using a NIST CO SRM with a concentration of 2500 ppm. The acceptance criteria for the predicted response versus the analyzer response with the 2500 ppm standard is a relative percent difference of <1%. Calibrator dilution checks must be conducted within 2 weeks of any assay.

13.4 Day of Assay Zero, Span, and Precision Check of Ambient Air Analyzers

On the day of each assay, each ambient air analyzer will be checked for precision and drift with 3 discrete analysis of a NIST SRM at a concentration of >80% of the instrument URL. Calculations of acceptability for these parameters will be done using the spreadsheets from the EPA Protocol method. The exact procedure is found in the working instructions presented in the Appendices.

13.5 Assay Gases

Gases accepted for assay must:

1. Have the concentration of gas certified by the vendor in accordance with the EPA-600/R-91/121 EPA Traceability Protocol.

2a. Contain CO at concentration ranges of 2500 – 10,000 ppm (for CO dilution standards) or 40-50 ppm (for direct CO standards), or

2b. SO2 and NO/NOx at concentrations of 25-100 ppm.

2c. Balance gas will be nitrogen.

3. Each cylinder accepted for assay must be accompanied with a copy of the original written certification report.

13.6 Assay Procedure

All assays of reference and candidate standards will be analyzed in 3 test sets, with each set consisting of all of the candidates standards, the primary SRM, and zero gas.

Cylinders will be run in a different order for each test set. All adjustments in dilution flow will be done with the diluent gas mass flow controller of the dilution calibrator. The pollutant mass flow controller will be set to a constant flow of 70 cc/min, with the exception of zero gas runs, where it will be set to 0.0 cc/min. Delivered gas concentrations will be >80% of the ambient air analyzers URL. Exact details of the assay procedure are presented in the working instructions, presented in the Appendices.

13.7 Quality Assurance Requirements

A table of the Quality Assurance requirements is presented below:

QA Parameter	QA Requirement
SRM Gas Standards (primary and check)	SRM certificate is not expired SRM pressure > 150 psig
Laboratory Flow Standard	Certified by NVLAP certified laboratory Certification is not expired
Dilution Calibrator	Flow calibrated within 2 weeks of assay Dilution check within 2 weeks of assay Flow error after calibration < 1%
Ambient Air Analyzer	Calibrated within 2 weeks of assay Estimate of Uncertainty <1% for assay range Analyzer calibration slope 0.98 - 1.02
Calibrator Dilution Check	Dilution check within 2 weeks of assay Dilution Check relative % difference <1%
Day of Assay Zero, Span, and Precision	Zero Check standard error <1% Zero Check accuracy within 5% Span standard error <1% Span accuracy within 5%
Candidate Standards	Standard error of assay <1% Error relative to vendor certificate <2% = acceptable Error relative to vendor certificate 2-4% = caution Error relative top vendor >4% = exceeds program limits

A detailed QA table is presented in the working instructions, presented in the Appendices

14.0 Calculations

The assay method as implemented consists of the written instructions and their accompanying EXCEL spreadsheets. All cylinder concentration calculations use the original worksheets developed for the EPA Protocol. Additional worksheets were added to the original protocol method to facilitate the quality assurance checks and procedural requirements in the EPA Protocol. Detailed instructions for using these worksheets is presented in the working instructions in the Appendices.

15.0 Data Reporting

There are 3 EXCEL workbooks, one for each pollutant; PGVP-CO, PGVP-SO2, and PGVP-NO/NOx. These workbooks are an integral part of the assay, and they are tightly integrated with the assay working instructions. The workbooks are the repository for all assay information, assay results and quality assurance information, Data will be reported from the analytical laboratory, via these worksheets, directly to OAQPS, which will disseminate this information to monitoring agencies providing gas cylinder standards for assay.

16.0 References

The EPA Traceability Protocol For Assay And Certification Of Gaseous Calibration Standards (EPA-600/R-97/121)

Working Instructions For Carbon Monoxide Assays For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

Working Instructions For Sulfur Dioxide Assays For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

Working Instructions For Oxides of Nitrogen For The Protocol Gas Verification Program In US EPA Region 2 (included in Appendix)

PGVP-CO EXCEL Workbook

PGVP-SO2 EXCEL Workbook

PGVP-NOx EXCEL Workbook

APPENDIX A:

WORKING INSTRUCTIONS

FOR

CARBON MONOXIDE ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 7

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Monitoring Management Branch
US EPA Region 2
2890 Woodbridge Avenue
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Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-CO v3.1.xls.** When using and/or archiving the PGVP-CO Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_C_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 -XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for CO data.

2.0 Assay Information Worksheet

The PGVP-CO Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: Flow calibrations are required within 2 weeks of any PGVP assay.

3.1 Materials Required

a. Environics 6103 Multi-gas Calibrator with 20 L/min diluent and 100 cc/min pollutant mass flow controllers (**MFC**s).

b. Filtered and pressure regulated air source capable of delivering 20 L/min at 30 psig. The air source must be capable of delivering flow to 2 ports at the same time.

c. BIOS Dfiner 220-H (0-30 L/min) and Definer 220-L (5-300 cc/min) flow cells and 9 pin data cable.

d. Laptop computer with Excel and BIOS Optimizer flow program and appropriate PGVP-xx workbooks.

e. Wrenches, 9/16” and 7/16” for working with ¼” and 1/8” Swagelok fittings.

f. ¼” Teflon tubing, 4’ length and terminated by ¼” Swagelok nut.

g. 1/8” Teflon tubing, 3’ length and terminated by a 1/8” Swagelok nut at one end. The other end is attached to a 2’ length of ¼” tubing via a Swagelok reducing union, and terminated by ¼” Swagelok nut.

h. ¼” and 1/8” Swagelok nuts, ferrules, and tee.

i. Phillips and flathead screw drivers.

j. Laboratory countdown timer.

k. Laboratory logbook and pens.

3.2 Environics 6103 Calibrator Setup and Gas Connections

3.2.1 Connect the outlets of the compressed air supply to **PORT 1** and **PORT 2** on the back of the calibrator. The air should not be turned on at this time.

3.2.2 Ensure that at least one of the **MANIFOLD OUTLET PORTS** is open to atmosphere.

3.2.3 Open the top lid of the Environics 6103 by removing the 4 screws on the top (the 2 screws on each of the side panels have been permanently removed), and lift the lid off the instrument.

3.2.4 On the right side panel, remove the rightmost and leftmost Phillips head screws. The right side panel will now open, as the bottom is hinged. Lay the right side panel down as flat as it goes.

3.2.5 Locate the diluent MFC. There are two MFC's located in the right front quadrant of the instrument. The diluent MFC can be identified by its position closer to the center and front of the instrument and the use of ¼" fittings. The MFC inlets are towards the rear of the instrument, and the outlet is toward the front.

3.2.6 Using a 9/16" wrench, remove the nut to the outlet of the diluent MFC.

3.2.7 Connect a 4' piece of ¼" Teflon with Swagelok nuts and ferrules to the diluent MFC outlet.

3.2.8 Turn on the Calibrator.

3.2.9 Turn on the compressed air supply to deliver 30 psi.

3.2.10 At the bottom of the LCD display, there will be 3 labels,

CONC FLOW PHOTO

directly above the 3 function switches (**F1, F2, F3**). Push **FLOW** (button **F2**).

3.2.11 Three new labels will appear on the bottom of the LCD Panel

START GAS EXIT.

Push **START** (button **F1**).

3.2.12 Three new labels will appear on the bottom of the LCD Panel

EDIT VIEW STOP.

Push **EDIT** (button **F1**).

3.2.13 Three new labels will appear on the bottom of the LCD Panel

UPDATE VIEW STOP.

The cursor will default to the top line, **AIR=0.0000 lpm**. On the keypad, enter 16.0.

3.2.14 Using the front panel arrow keys, move the cursor one row down to **CO=0.0000 ccm**. Enter 78.0 on the numerical keypad and push **UPDATE** (button **F1**). The calibrator will accept the changes and return to the display seen in section 3.2.12.

Note: The Environics 6103 has a solenoid that cuts off all flow to both MFCs if there is no pressure at the diluent flow controller. Therefore, there must be flow present at the diluent MFC at the same time in order for zero air to flow to the pollutant gas flow controller, thus requiring the need for 2 compressed air inputs.

3.2.15 The front panel LCD should now indicate flow for both MFCs. Press **MENU** on the front panel. The LCD display will show:

O3 CONTROL = DISABLED
PHO SOURCE = EXTERNAL
PHO PUMP = OFF
O3 CTRL PHOSRC PUMP

Front panel buttons F1, F2, or F3 correspond to the parameters of O3 control, photometer source, and the photometer pump, respectively. If the display does not show the parameters shown above, push the function button corresponding to the parameter that needs correction and toggle it to the correct value. Push the **MENU** button to accept these changes and go back to the default run display.

Note: The screen for O3 control, photometer source, and the photometer pump can only be called up after pressing START, as was done in step 3.2.11.

3.2.16 Let the calibrator equilibrate for a minimum of one hour prior to taking measurements.

3.3 BIOS DEFINER 220 Setup and Flow connections

3.3.1 Open the inlet and outlet caps of the Definer 220.

3.3.2 Plug in the DEFINER 220 to the wall outlet and press **ON**.

3.3.3 The front panel will display:

MEASURE | SETUP

Using the arrow keys on the front panel, toggle the cursor one step down to **SETUP** and press enter.

3.3.4 The LCD display will show:

●Readings	**●Preferences**
●Units	**●Power**
●Time	**●Diagnostics**
●Date	**●About**

MEASURES

Using the arrow keys on the front panel, toggle the cursor one step down to **Readings** and press enter.

3.3.5 The LCD display will show:

Type: Std
Number in Average: 010
Time Between: 00 min
Sensor Factor: 1.000

CONFIRM | EXIT

If the **Type, Number in Average, Time Between or Sensor factor** do not read these values, consult the DEFINER 220 Manual to adjust these parameters to these values. Using the arrow keys on the front panel, toggle the cursor one step down to **CONFIRM** and press enter to back to the **Setup** menu. Using the arrow keys on the front panel, toggle the cursor one step down to **Units** and press enter.

3.3.6 The LCD display will show:

Flow in: scc/min
Pressure: mmHg
Temp: C
StdTo: 25.0 C

CONFIRM | EXIT

If the **Flow in, Pressure, Temp and StdTo** do not register these units, consult the DEFINER 220 Manual to adjust these parameters to these units. Using the arrow keys on the front panel, toggle the cursor one step down to **CONFIRM** and press enter to back to the **Setup** menu. Using the arrow keys on the front panel, toggle the cursor one step down to **Time** and press enter.

3.3.7 The LCD display will show:

Hour: xx
Minutes: yy
Format: PM or AM

CONFIRM | EXIT

If the **Hour, Minutes** and **Format** corresponding to the current time is not correct, consult the DEFINER 220 Manual to adjust to the correct time. Using the arrow keys on the front panel, toggle the cursor one step down to **CONFIRM** and press enter to back to the **Setup** menu. Using the arrow keys on the front panel, toggle the cursor one step down to **Date** and press enter.

3.3.8 The LCD display will show:

Month: MM
Date: DD
Year: YYYY
Format: MM-DD-YYYY

CONFIRM | EXIT

If the **Month, Date, Year** and **Format** corresponding to the current date is not correct, consult the DEFINER 220 Manual to adjust to the correct date. Using the arrow keys on the front panel, toggle the cursor one step down to **CONFIRM** and press enter to back to the **Setup** menu. Using the arrow keys on the front panel, toggle the cursor to **Preferences** and press enter.

3.3.9 The LCD Display will show:

Read Default: Continuous
Magnification: Detail
Default Settings: No

CONFIRM | EXIT

If the **Read Default, Magnification, and Default Settings** do not read these settings, consult the DEFINER 220 Manual to adjust these parameters to these settings. Using the arrow keys on the front panel, toggle the cursor one step down to **CONFIRM** and press enter to back to the **Setup** menu. Using the arrow keys on the front panel, toggle the cursor down to **MEASURE** and press enter. The instrument is now ready for use.

3.3.10 Connect the tubing attached to the Environics 6103 diluent MFC output to the Swagelok fitting on the pressure side of the DEFINER 220.

3.3.11 Toggle the cursor to **CONT.** on the DEFINER 220 front panel and hit enter. The piston will start to move, and the DEFINER 220 will start to display flow readings.

3.4 Computer Setup and Data Logging for Flow Calibration

3.4.1 Connect the 9 pin data cable to the BIOS DEFINER 220 and the laptop computer.

3.4.2 Start the computer, and launch the BIOS Optimizer program.

3.4.3 Click on the LOGIN icon in the upper left hand corner of the program. The user and password window will open.

3.4.4 Enter **biosadmin** for the user name and **bios** for the password. Use lower case for entering the information.

3.4.5 In the DATA STREAM FILE LOCATION window at the top of the program enter **C:\BIOS data\YYYY-MM-DD PGVP Environics 6103.txt**, where **YYYY-MM-DD** denotes the date of calibration in year-month-day format.

3.4.6 Press the **start** button in the Optimizer program. Data will be collected and a chart will be generated in the program showing all data points collected.

3.4.7 Start a new page in the PGVP laboratory logbook and enter the current date and time, and a heading of “Environics 6103 flow calibration”.

3.5 Environics 6103 Diluent MFC Calibration

Note: The Environics 6103 calibrator must be warmed up at 16 L/min for the diluent flow and 78 cc/min for the pollutant flow for 60 minutes prior to the start of the calibration per the instructions in section 3.2. The DEFINER 220 flowmeter should already be collecting data for the diluent flow controller as per section 3.4.

3.5.1 Ensure that the Environics 6103 diluent MFC is set to 16.0 L/min. Set the timer for 20 minutes and wait until the timer indicates that the time has elapsed.

3.5.2 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.2.

3.5.3 Set the flow of the Environics 6103 diluent MFC to 12.0 L/min. Setting of flows has been specified in section 3.2.

3.5.4 Set the timer for 20 minutes.

3.5.5 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.5.

3.5.6 Set the flow of the Environics 6103 diluent MFC to 8.0 L/min.

3.5.7 Set the timer for 20 minutes.

3.5.8 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.8.

3.5.9 Set the flow of the Environics 6103 diluent MFC to 6.0 L/min.

3.5.10 Set the timer for 20 minutes.

3.5.11 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.11.

3.5.12 Set the flow of the Environics 6103 diluent MFC to 4.0 L/min.

3.5.13 Set the timer for 20 minutes.

3.5.14 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.5.14. This is the last measurement for the diluent MFC.

3.5.15 Detach the 4’ Teflon line from the DEFINER 220 and the diluent MFC output and reattach the Environics ¼” fitting removed in step 2.2.6 to the output of the diluent MFC.

3.6 Environics 6103 Pollutant MFC Calibration

3.6.1 Remove the 1/8” Swagelok fitting from the pollutant MFC output. The output is found on the end of the pollutant MFC closer to the front panel of the calibrator.

3.6.2 Locate the 1/8” tubing referred to in step 2.1. Attach the 1/8” nut to the output of the pollutant MFC.

3.6.4 Cap the inlets and outlets of BIOS DEFINER 220-H, and remove the inlet and outlet caps on BIOS DEFINER 220-L.

3.6.5 Attach the tubing from the pollutant MFC outlet to the Swagelok fitting on the pressure side of the DEFINER 220-L.

3.6.6 Move the cursor of the DEFINER 220-L LCD panel to **CONT.** and push **ENTER.** The piston will start to move as a flow rate of 78 cc/min was programmed for the pollutant MFC previously in step 3.2.14.

3.6.7 Set the timer for 20 minutes.

3.6.8 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.8.

3.6.9 Set the flow of the Environics 6103 pollutant MFC to 70.0 cc/min.

3.6.10 Set the timer for 20.

3.6.11 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.11.

3.6.12 Set the flow of the Environics 6103 pollutant MFC to 60.0 cc/min.

3.6.13 Set the timer for 20.

3.6.14 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.14.

3.6.15 Set the flow of the Environics 6103 pollutant MFC to 50.0 cc/min.

3.6.16 Set the timer for 20.

3.6.17 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.17.

3.6.18 Set the flow of the Environics 6103 pollutant MFC to 40.0 cc/min.

3.6.19 Set the timer for 20.

3.6.20 If a stable trace has been established (defined as variability of less than 0.5% over a period of the last 10 minutes of measurement), record the Environics set point, reading, and the average flow as indicated in the BIOS Optimizer data sheet in the laboratory logbook. Final flows will be determined when working with the downloaded data set from all runs. If a stable reading has not been achieved, reset the timer for 20 minutes and repeat step 3.6.20. This is the last point in the pollutant MFC calibration.

3.6.21 Detach the Teflon line from the DEFINER 220 and the pollutant MFC output and reattach the Environics 1/8" fitting removed in step 3.6.1 to the output of the diluent MFC.

3.6.22 Replace the lid of the Environics 6103 and reattach the 4 screws that were removed in step 3.2.3.

3.7 Flow Calculations/Completion of the Calibrator Flow Cal Worksheet

Note: Flow calibrations of the Environics 6103 by default utilize the PGVP-CO workbook. For SO2 and NO/NOx assays the data collected in this worksheet is copied and pasted into the respective PGVP-SO2 and PGVP-NOx workbooks. Copying and pasting procedures are given in the respective SO2 and NO/NOx, workbooks.

3.7.1 In the PGVP-CO workbook, open the Calibrator Flow Cal worksheet.

3.7.2 Data collected during the flow calibration must be transferred to the Calibrator Information block. Click the **DATA** tab on the top Excel menu bar, scroll down the drop down menu to **IMPORT EXTERNAL DATA**, and highlight **IMPORT DATA**. The **SELECT DATA SOURCE** window will open.

Note: If the IMPORT DATA window is grayed out, it is because the source data definitions from a previous use are still defined. To clear this select DATA → IMPORT EXTERNAL DATA → DATA RANGE PROPERTIES. This will open up the EXTERNAL DATA RANGE PROPERTIES window. Uncheck the box SAVE QUERY DEFINITION. This will open a dialog box requesting to permanently delete the query definition. Click OK. This will close the dialog box. Then click OK on the EXTERNAL DATA RANGE PROPERTIES WINDOW. Now you can restart at the beginning of this step to import data.

3.7.3 In the **SELECT DATA SOURCE** window, click on the drop down menu at the top and highlight the file previously selected for storing the BIOS flow data in section 3.4.5 (**C:\BIOS data\XXXX-XX-XX PGVP Environics 6103.txt**). The **TEXT IMPORT WIZARD STEP 1 OF 3** window will open.

3.7.4 Select the **DELIMITED** radio button. The other defaults, **START IMPORT AT ROW 1** and FILE **ORIGIN 437: OEM United States**, should be left as is. In the lower half of the window will be the path length to the selected file as well as a limited preview of the file selected.

3.7.5 Click the **NEXT** button. The TEXT **IMPORT WIZARD STEP 2 OF 3** window will open.

3.7.6 In the **DELIMITER** block put a check mark by the **COMMA** field. Uncheck any other selected delimiters.

3.7.7 Click **NEXT**. The **TEXT IMPORT WIZARD STEP 3 OF 3** window will open.

3.7.8 Click **FINISH**. The **IMPORT DATA** window will open.

3.7.9 In the **IMPORT DATA** window, the **EXISTING WORKSHEET** radio button should be highlighted (this is the default) and the window below it should already be highlighted and read **=$A$1**. Enter **=$M$48** in the highlighted window and click **OK**. The window will close and the BIOS flow data will be imported into the Calibrator Flow Cal worksheet starting at cell M48.

3.7.10 The Calibrator Flow Cal worksheet consists of 4 blocks. In the first block, Calibrator Information, enter the calibration date and any notes. These fields are highlighted in yellow. The other fields in this block, Manufacturer, Model #, and Serial # will automatically be filled in, as these data are carried over from the Assay Information worksheet. The yellow highlighted fields are exported automatically to the Assay Information worksheet, in the Gas Dilution Calibrator block.

3.7.11 The second block in the Calibrator Flow Cal worksheet is Flow Standard Information. All the blocks should already be filled in, as the information is obtained from the Assay Information worksheet automatically.

3.7.12 The third block in the Calibrator Flow Cal worksheet is Flow Calibration. The calibration date in the header of this block is taken automatically from cell B5. Enter the set points and Environics 6103 readings obtained for the diluent MFC into cells B20..B24 and C20..C24, respectively. These data were recorded in the laboratory logbook in section 3.5 above.

3.7.13 Enter the set points and Environics readings obtained for the pollutant MFC flow into cells G20..G24 and H20..H24, respectively. These data were recorded in the laboratory logbook in section 3.6 above.

3.7.14 Place the cursor on, and highlight, cell D20, the first entry in the column for Actual Flow, and shaded yellow. Type the following formula:

=AVERAGE(Mxx..Myy)

Where: **xx** = is the last flow taken at 16.0 L/min
yy = the flow taken 10 minutes earlier

Hit **ENTER.** Cell row M is where the individual BIOS DEFINER 220 flows were recorded. Cell Row Z shows the time the data point was taken. We are taking the average flow over the last 10 minutes of calibration.

3.7.15 Place the cursor on cell D21 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 12.0 L/min for **xx**, and the 12.0 L/min point taken 10 minutes earlier for **yy**.

3.7.16 Place the cursor on cell D22 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 8.0 L/min for **xx**, and the 8.0 L/min point taken 10 minutes earlier for **yy**.

3.7.17 Place the cursor on cell D23 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 6.0 L/min for **xx**, and the 6.0 L/min point taken 10 minutes earlier for **yy**.

3.7.18 Place the cursor on cell D24 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 4.0 L/min for **xx**, and the 4.0 L/min point taken 10 minutes earlier for **yy**.

3.7.19 Place the cursor on cell I20 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 78.0 cc/min for **xx**, and the 78.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.20 Place the cursor on cell I21 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 70.0 cc/min for **xx**, and the 70.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.21 Place the cursor on cell I22 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 60.0 cc/min for **xx**, and the 60.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.22 Place the cursor on cell I23 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 50.0 cc/min for **xx**, and the 50.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.23 Place the cursor on cell I24 and repeat the process and formula outlined in step 3.7.14 substituting the last flow taken at 40.0 cc/min for **xx**, and the 40.0 cc/min point taken 10 minutes earlier for **yy**.

3.7.24 The Flow Calibration block will now show the slope and intercept for both MFCs.

3.7.25 The Curve Predicted columns in the Flow Calibration block are calculated by the formula:

CURVE PREDICTED VALUE = (MFC SETTING x SLOPE) – INTERCEPT

3.7.26 The % error in curve prediction is calculated by the formula:

(CURVE PREDICTED VALUE – ACTUAL FLOW)/(ACTUAL FLOW)

3.8 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 48i CO Analyzer Calibration Procedure & Analyzer Cal Worksheet

Note: The CO analyzer is set to a range of 50 ppm CO.

Note: The CO analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: The procedure for setting flow rates for Environics 6103 was described in section 3.2 and therefore will not be repeated here.

4.1 Required Materials

a. Thermo 48i ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 5,000 ppm CO SRM and CGA 350 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-CO workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to CO Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the 1/4" output line from the Environics 6103 to the glass CO manifold. The CO analyzers are by default plumbed to the glass manifold via ¼" Teflon lines. The exhaust of the manifold is vented via a ½" line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the CO manifold. Let the CO analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 48i CO analyzer(s).

4.2.6 Install the CGA 350 regulator on the 5,000 ppm CO SRM cylinder. The cylinder should be charged overnight according to the following procedure.

a. Turn the delivery valve of the pressure regulator to the closed position.

b. Turn the cylinder valve of the CO SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

c. Set the pressure regulator delivery pressure for 30 psi.

d. Close the cylinder valve. The pressure regulator will remain under pressure.

e. Check to verify that the SRM cylinder valve is closed.

f. Let cylinder and regulator equilibrate overnight.

4.2.7 Purge the CO SRM regulator according to the following procedure:

a. Attach a 1/2" delivery line to the pressure regulator connected to the CO SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.2.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the CO SRM to Port 2 of the Environics 6103.

4.2.9 Open the CO SRM cylinder valve, and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Thermo 48i CO Analyzer Zero and Span

4.4.1 Set the Environics 6103 diluent MFC to 8.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 48i 10 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel and align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **BKG** and **COEF** displayed on the Thermo 48i front panel in the laboratory logbook under the heading Thermo 48i Pre Calibration Background & CO Coefficient Readings. After taking the readings, push the **RUN** button on the Thermo 48i front panel.

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 48i display will show a new window with the cursor defaulting to the **CAL BACKGROUND** line. Press **ENTER.** A new window will be displayed on the Thermo 48i displaying the current instrument reading and the question **SET CO TO ZERO?** Press **ENTER** a 2nd time to zero the instrument. After setting the zero, push the **RUN** button on the Thermo 48i front panel.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 8.0 L/min.

4.4.6 Allow the Thermo 48i to sample the Environics 6103 output for 15 minutes.

4.4.7 During this waiting period, open the Excel PGVP-CO Workbook that will be used for this batch of CO assays. The file naming conventions have been outlined in step 1.0. Open the Analyzer Cal worksheet and enter 8000 in cell B13, the High MFC Device Setting. Cell F13 will display the delivered CO concentration at the current conditions (Environics 6103 set for 8.0 L/min diluent and 78.0 cc/min pollutant gas using the 5,000 ppm CO SRM).

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4.4.8 After a steady trace is observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 48i display will show a new window with the cursor defaulting to the **CAL BACKGROUND** line. Using the front panel arrow keys, place the cursor in front of the **CAL COEF** line and press **ENTER.** A new window will be displayed on the Thermo 48i displaying the current instrument reading, analyzer range in ppm, and the line **SET TO 000XX.X00?** Using the arrow buttons on the front panel of the Thermo 48i, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered CO concentration specified in cell F13 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **RUN** button to get to the main screen of the Thermo 48i.

4.4.9 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.10 During the waiting period for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel, align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **BKG** and **COEF** displayed on the Thermo 48I front panel in the laboratory logbook under the heading Thermo 48i Post Calibration Background & CO Coefficient Readings. After taking the readings, push the **RUN** button to return to the Thermo 48i main screen.

4.4.11 After a steady trace is observed , record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading Post Calibration Zero.

4.5 Thermo 48i Calibration for the CO Assay using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the Analyzer Cal worksheet from the Assay Info and Calibrator Flow Cal worksheets.

4.5.1 In the Analyzer Cal worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 15 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G13 (analyzer response)of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G14 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 15 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G15 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 15 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G16 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 15 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G17 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average CO concentration from the ENVIDAS software in cell G18 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

4.6.1 In the Analyzer Cal worksheet collect the delivered CO concentration and analyzer response: highlight cells F13..G18 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the calibration data for the CO analyzer into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F13 in the Analyzer Cal Worksheet (analyzer response) → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ copy. Go to the Analyzer Cal worksheet cell I13 → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F14..F17 (one cell at a time), recording the results in cells I14..I17, respectively.

4.6.7 The analyzer estimate of uncertainty must be less than 1% for the Thermo 48i to be considered well characterized at that concentration, and thus allowing the analyzer to be used for CO cylinder assays.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires 2 SRMs of different concentrations. For this method the 5,000 ppm CO SRM is referred to as the primary SRM and the 2,500 ppm CO SRM is referred to as the check SRM.

Note: The dilution check is done using the PGVP-CO workbook, Calibrator Dilution Check worksheet. If the Environics 6103 calibrator passes this check it is considered qualified for the SO2 and NO/NOX assays. Data from this sheet is then copied to the PGVP-SO2 and PGVP-NOX for their respective assays.

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

Note: The dilution check must be done with a CO analyzer that has been running for at least 3 hours, and preferably overnight sampling zero air. The CO SRM cylinders to be used should have equilibrated regulators as defined in section 4.2.6. The Environics 6103 calibrator should be warmed by running for at least an hour prior to starting this procedure.

5.1 Required Materials

This section requires all the materials enumerated in Section 4.1, plus a second CO SRM of 2,500 ppm (the SRM check standard)

5.2 Dilution Leak Check Procedure & Worksheet

5.2.1 Open the PGVP-CO workbook for the current assays and open the Calibrator Dilution Check workbook.

> **Note: All non shaded cells have their values automatically entered into the Calibrator Dilution Check worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.**

5.2.2 Enter the current date in cell B6, and any notes in cell I6.

5.2.3. Ensure that the ENVIDAS software is logging the Thermo 48i output data stream.

5.2.4 Set the Environics 6103 diluent MFC to 8.0 L/min.

5.2.5 Set the Environics 6103 pollutant MFC to 0.0 cc/min.

5.2.6 Connect the output of the Environics 6103 to the CO Glass manifold. The CO analyzer(s) are by default connected to this glass manifold.

5.2.7 Purge the regulator of the Primary CO-SRM, per the procedures outlined in section 4.2.7

5.2.8 Connect the output of the Primary CO SRM regulator to port 2 of the Environics 6103, and open the cylinder valve and regulator valve of the Primary CO SRM.

5.2.9 Set the Environics 6103 pollutant MFC to 70.0 cc/min and set the timer to 15 minutes.

5.2.10 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D23 of the Calibrator Dilution Check worksheet.

5.2.11 After the timer has beeped, and a steady trace has been achieved (defined as a reading not varying by more than 0.2 ppm over a 5 minute period), record the CO concentration from the ENVIDAS software 5 minute average in cell J23 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.12 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.13 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D24 of the Calibrator Dilution Check worksheet.

5.2.14 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J24 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.15 Shut the regulator valve and then the cylinder valve of the Primary CO SRM. Disconnect the Primary CO SRM from Port 2 of the Environics 6103.

5.2.16 Purge the regulator of the Check CO SRM per the instructions in step 4.2.7..

5.2.17 Connect the check CO-SRM to port 2 of the Environics 6103 and open the cylinder valve and the regulator valve.

5.2.18 Set the Environics diluent MFC to 4.0 L/min, and the pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

5.2.19 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D25 of the Calibrator Dilution Check worksheet

5.2.20 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J25 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.21 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.22 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D26 of the Calibrator Dilution Check worksheet

5.2.23 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J26 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.24 Set the Environics pollutant MFC to 70.0 cc/min The diluent MFC should still be at 4.0 L/min.. Set the timer for 15 minutes.

5.2.25 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D27 of the Calibrator Dilution Check worksheet

5.2.26 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J27 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.27 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.28 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D28 of the Calibrator Dilution Check worksheet

5.2.29 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J28 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.30 Set the Environics pollutant MFC to 70.0 cc/min The diluent MFC should still be at 4.0 L/min.. Set the timer for 15 minutes.

5.2.31 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D29 of the Calibrator Dilution Check worksheet

5.2.32 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J29 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook

5.2.33 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

5.2.34 During the waiting period, enter the diluent MFC flow rate (4,000), in cell D30 of the Calibrator Dilution Check worksheet

5.2.35 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J30 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.2.36 Set the Environics 6103 diluent MFC to 8.0 L/min, and the pollutant MFC to 70.0 cc/min. Set the timer to 15 minutes.

5.2.37 During the waiting period, enter the diluent MFC flow rate (8,000), in cell D31 of the Calibrator Dilution Check worksheet.

5.2.38 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J31 of the Calibrator Dilution Check worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

5.3 Calibrator Dilution Check Worksheet Evaluation

5.3.1 The Calibrator Dilution Check worksheet imports or calculates all data in the non shaded cells by obtaining the information from the Assay Information, Calibration Flow Cal, and Analyzer Calibration worksheets previously entered in the PGVP-CO workbook.

5.3.2 In order for the Environics 6103 to qualify for use in PGVP gas assays, the requirement from the EPA Protocol requires a relative % difference of < 1% calculated as follows:

$$\text{Relative \% difference} = (100)*\left(\frac{\text{mean analyzer Check SRM response} - \text{Predicted Response}}{\text{Predicted Response}}\right)$$

5.3.3 The mean response to the Check SRM is calculated in the Calibration Dilution Check worksheet in cell J32.

5.3.4 The predicted instrument response for the CO Check SRM is calculated in the Calibration Dilution Check worksheet in cell I26 (and I28 and I30), by determining the delivered CO concentration from the Environics 6103 settings and flow calibration and plugging this value into the Thermo 48i CO analyzer calibration results.

5.3.5 The calculation of relative % difference is given in cell D33 of the Calibration Dilution Check worksheet.

5.3.6 If the relative % difference is less than 1% the instrument has been qualified for use in CO, SO2, and NOx assays for a period of 2 weeks.

5.3.7 At the conclusion of this test, close all SRM gas cylinder valves, and run zero air through the Environics 6103 and the CO analyzer.

5.3.8 Save all data from the ENVIDAS data logging system and the PGVP worksheet.

6.0 Day of Assay Zero, Span, and Precision Procedure and Day of Assay Zero & Span Worksheet

Note: Standard Procedure in Region 7 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-CO workbook for the current assay and open the Day of Assay Zero and Span worksheet.

Note: All non shaded cells have their values automatically entered into the Day of Assay Zero and Span worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 48i output data stream.

6.2.3 Equilibrate the regulator on the Primary CO SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 48i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary CO SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the carbon monoxide glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 8.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 8,000 in the High MFC Device Setting column in cells D17..D22.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J17 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J18 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J19 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J20 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J21 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 15 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the CO concentration from the ENVIDAS software 5 minute average in cell J22 of the Day of Analysis Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Analysis Zero and Span Worksheet Finalization and Evaluation

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-CO Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

6.3.1 In the Day of Analysis Zero and Span worksheet, collect the response to zero gas: control-left click on cells J17, J19, and J21 → right click → copy.

6.3.2 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.3 Select the Day of Analysis Zero and Span worksheet, collect the predicted CO response: press escape → left click on cells H18 → control-left click on H20, and H22 → right click → copy.

6.3.4 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.5 Select the Day of Analysis Zero and Span worksheet, collect the analyzer CO concentration: press Escape → left click on cell J18 → control-left click on J20, and J22 → right click → copy.

6.3.6 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.3.8 Select the Day of Analysis Zero and Span worksheet → select cell D26 → right click → paste special → values → OK.

6.3.9 In the Day of Analysis Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D28 and D30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.10 In the Day of Analysis Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F28 and F30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.11 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 Carbon Monoxide Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary CO SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-CO workbook for the current assay and open the Assay Worksheet.

Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 48i output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 48i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary CO SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 to the carbon monoxide glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 48i CO analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-50 ppm. With challenge standard cylinder concentrations of 2500 – 10,000 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart					
Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
CO	10000	10,000	16.0	70	43.56
	5000	10,000	8.0	70	43.37
	2500	10,000	4.0	70	43.00

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (8,000) in cell F8 of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.2 ppm over a 5 minute period) record the CO concentration from the ENVIDAS software 5 minute average in cell L8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The CO 5,000 ppm primary SRM should already be attached to the Environics 6103 (section 7.2 above), and the regulator should have already been purged (section 7.2). Set the timer for 15 minutes.

7.4.6 During the waiting time, write the diluent MFC settings (8,000) in cell F9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the CO concentration from the ENVIDAS software 5 minute average in cell L9, the Assay Worksheet. Record the Environics MFC settings and analyzer output in the logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 10 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary CO SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve a CO reading between 40-45 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 15 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (8,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the CO concentration from the ENVIDAS software 5 minute average in cell L10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows and CO analyzer readings should be entered in ranges F11..F14, and L11..L14, respectively for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range F20..F26, and analyzer results will be placed in cell range L20..L26.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range F32..F38, and analyzer results are reported in cell range L32..L48.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed Concentrations and Finalization of Assay Worksheet.

Note: This portion of the SOP will calculate the final concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

7.7.1 Scroll to cell R42 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.2 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.3 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → paste special → values → OK.

7.7.4 **For challenge standard #1**: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.5 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S70 → right click → paste special → values → OK.

7.7.6 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U94 → right click → paste special → values → OK.

7.7.7 **For challenge standard #2**: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.8 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V70 → right click → paste special → values → OK.

7.7.9 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X94 → right click → paste special → values → OK.

7.7.10 **For challenge standard #3**: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.11 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y70 → right click → paste special → values → OK.

7.7.12 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA94 → right click → paste special → values → OK.

7.7.13 For challenge standard #4: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.14 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB70 → right click → paste special → values → OK.

7.7.15 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD94 → right click → paste special → values → OK

7.7.16 For challenge standard #5: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.17 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → right click → copy. → go to the Assay Worksheet, highlight Cell AE70 → right click → paste special → values → OK.

7.7.18 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG94 → right click → paste special → values → OK

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-CO workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step These are the various analytical steps taken to conduct this assay.

QA Requirement Quality Assurance requirements are derived from the EPA Protocol

Result These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.

Status A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a “warning” level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-CO workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

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APPENDIX B:

WORKING INSTRUCTIONS

FOR

SULFUR DIOXIDE ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 7

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Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-SO2 v3.1.xls.** When using and/or archiving the PGVP-CO Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_S_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 -XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for SO2 data.

2.0 Assay Information Worksheet

The PGVP-SO2 Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: Flow calibrations are required within 2 weeks of any PGVP assay.

3.1 Calibration Procedure

The Environics 6103 calibration procedure is detailed in the Working Instructions for Carbon Monoxide Assays, and is not reproduced here. Current Environics 6103 flow calibration data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-SO2) in order to use the current calibration. The procedure for copying this data is as follows:

3.1.1 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet, highlight cell range B3..K28.

3.1.2 Select edit from the menu bar → clear→ all.

3.1.3 Go to the PGVP-CO workbook, Calibrator Flow Cal worksheet, → highlight cell range B1..K26 → right click → copy.

3.1.4 Select the PGVP-SO2 workbook, Calibrator Flow Cal worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

3.1.5 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet, delete all cells with data from row N50 and below.

3.1.6 Select the PGVP-CO workbook, Calibrator Flow Cal worksheet, highlight all cells with data commencing with cell N48 and below → right click →copy

3.1.7 In the PGVP-SO2 workbook, Calibrator Flow Cal worksheet → highlight cell N50 → right click → paste.

3.1.8 Close the PGVP-CO workbook that was used.

3.2 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and

intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 43i SO2 Analyzer Calibration Procedure & Analyzer Cal Worksheet

Note: The SO2 analyzer is set to a range of 0.500 ppm SO2.

Note: The SO2 analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: Initial upscale points require 60 minutes for SO2 equilibration. Later points require a 20 minute equilibration time

Note: The procedure for setting flow rates for the Environics 6103 is described in the Working Instructions for Carbon Monoxide Assays, Section 3.2, will not be repeated here.

4.1 Required Materials

a. Thermo 43i ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 100 ppm SO2 SRM and CGA 660 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-CO workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to SO2 Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn the on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the ½” output line from the Environics 6103 to the glass SO2 manifold. The SO2 analyzers are by default plumbed to the glass manifold via ¼” Teflon lines. The exhaust of the manifold is vented via a ½” line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the SO2 manifold. Let the SO2 analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 43i SO2 analyzer(s).

4.2.6 Install the CGA 660 regulator on the 100 ppm SO2 SRM cylinder. The cylinder should be charged overnight according to the following procedure.

g. Turn the delivery valve of the pressure regulator to the closed position.

h. Turn the cylinder valve of the SO2 SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

i. Set the pressure regulator delivery pressure for 30 psi.

j. Close the cylinder valve. The pressure regulator will remain under pressure.

k. Check to verify that the SRM cylinder valve is closed.

l. Let cylinder and regulator equilibrate overnight.

4.2.7 Purge the SO2 SRM regulator according to the following procedure:

a. Attach a ¼” delivery line to the pressure regulator connected to the SO2 SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.2.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the SO2 SRM to Port 2 of the Environics 6103.

4.2.9 Open the SO2 SRM cylinder valve and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Thermo 43i SO2 Analyzer Zero and Span

4.4.1 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 43i 20 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button (it is the 2nd button down, on the left hand side of the analyzer and it has a page icon printed on it), and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER** (the enter button has a return icon printed on it and it is centered between the 4 directional arrow buttons used to move the cursor)**.** Record the **SO2 BKG** and **SO2 COEF** displayed on the Thermo 43i LCD in the laboratory logbook under the heading Thermo 43i Pre Calibration Background & SO2 Coefficient Readings. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 43i analyzer, and designated by a right pointing solid triangle icon).

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** A new screen will appear on the LCD with the cursor pointing to **CAL SO2 BACKGROUND**. Press **ENTER.** The Thermo 43i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET SO2 TO ZERO.** Press **ENTER.** After setting the zero, push the **RUN** button on the Thermo 43i front panel.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 16.0 L/min.

4.4.6 Allow the Thermo 43i to sample the Environics 6103 output for 60 minutes.

4.4.7 During this waiting period, open the Excel PGVP-SO2 Workbook that will be used for this batch of SO2 assays. The file naming conventions have been outlined in Section 1.0. The Assay Information worksheet should have already been filled out as per steps 2.0.

4.4.8 Go to the Analyzer Cal worksheet and enter 16000 in cell B13, the High MFC Device Setting. Cell F13 will display the delivered SO2 concentration at the current conditions (Environics 6103 set for 16.0 L/min diluent and 78.0 cc/min pollutant gas using the 100 ppm SO2 SRM).

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4.4.9 After the 60 minute waiting period and a steady data trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 43i display will show a new window with the cursor defaulting to the **CAL SO2 BACKGROUND** line. Using the front panel arrow keys, place the cursor in front of the **CAL SO2 COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.10 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered SO2 concentration specified in cell F13 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **RUN** button to get to the main screen of the Thermo 43i.

4.4.11 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.12 During the waiting period for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel, align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **SO2 BKG** and **SO2 COEF** displayed on the Thermo 43i front panel in the laboratory logbook under the heading Thermo 43i Post Calibration Background & SO2 Coefficient Readings. After taking the readings, push the **RUN** button to return to the Thermo 43i main screen.

4.4.13 After a steady trace is observed, record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading Post Calibration Zero.

4.5 Thermo 43i Calibration for the SO2 Assay Using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the Analyzer Cal worksheet from the Assay Info and Calibrator Flow Cal worksheets.

4.5.1 In the Analyzer Cal worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 20 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G13 (analyzer response) of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G14 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 20 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G15 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 20 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G16 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 20 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G17 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average SO2 concentration from the ENVIDAS software in cell G18 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

4.6.1 In the Analyzer Cal worksheet collect the delivered SO2 concentration and analyzer response: highlight cells F13..G18 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the calibration data for the SO2 analyzer into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F13 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I13 → right click → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F14..F17 (one cell at a time), recording the results in cells I14..I17, respectively.

4.6.7 The analyzer estimate of uncertainty must be less than 1% for the Thermo 43i to be considered well characterized at that concentration, and thus allowing the analyzer to be used for SO2 cylinder assays.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires assay of 2 SRMs of the same compound with different concentrations

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

5.1 Dilution Check Procedure

The Environics 6103 dilution check procedure is detailed in the Working Instructions for Carbon Monoxide Assays, Section 5.0, and is not reproduced here. Current Environics 6103 dilution check data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-SO2) in order to use the current calibration. The procedure for copying this data is as follows:

5.1.1 In the PGVP-SO2 workbook, Calibrator Dilution Check worksheet, highlight cell range B3..K35.

5.1.2 Select edit from the menu bar → clear→ all.

5.1.3 Go to the PGVP-CO workbook, Calibrator Dilution Check worksheet, → highlight cell range B2..K34 → right click → copy.

5.1.4 Select the PGVP-SO2 workbook, Calibrator Dilution Check worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

5.1.5 Close the PGVP-CO workbook that was used.

6.0 Day of Assay Zero, Span, and Precision Procedure and <u>Day of Assay Zero & Span</u> Worksheet

Note: Standard Procedure in Region 2 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-SO2 workbook for the current assay and open the <u>Day of Assay Zero and Span</u> worksheet.

Note: All non shaded cells have their values automatically entered into the <u>Day of Assay Zero and Span</u> worksheet from the <u>Assay Info,</u> <u>Calibrator Flow Cal</u>, and <u>Analyzer Cal</u> worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 43i output data stream.

6.2.3 Equilibrate the regulator on the Primary SO2 SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 43i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary SO2 SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the sulfur dioxide glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 16,000 in the High MFC Device Setting column in cells D17..D22.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J17 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 60 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J18 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J19 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J20 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J21 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the SO2 concentration from the ENVIDAS software 5 minute average in cell J22 of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Assay Zero and Span Worksheet Finalization and Evaluation

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-SO2 Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

6.3.1 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J17, J19, and J21 → right click → copy.

6.3.2 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.3 Select the Day of Assay Zero and Span worksheet, collect the predicted SO2 response: press escape → left click on cells H18 → control-left click on H20, and H22 → right click → copy.

6.3.4 Select cell E233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.5 Select the Day of Assay Zero and Span worksheet, collect the analyzer SO2 concentration: press Escape → left click on cell J18 → control-left click on J20, and J22 → right click → copy.

6.3.6 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.3.8 Select the Day of Assay Zero and Span worksheet → select cell D26 → right click → paste special → values → OK.

6.3.9 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D28 and D30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.10 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F28 and F30, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.7 above.

6.3.11 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 SO2 Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary SO2 SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-SO2 workbook for the current assay and open the Assay Worksheet.

Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 43i output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 43i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary SO2 SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 the sulfur dioxide glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 43i SO2 analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-0.500 ppm. With challenge standard cylinder concentrations of 25 – 100 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart

Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
SO2	100	100	16.0	70	0.433
	50	100	8.0	70	0.432
	25	100	4.0	70	0.430

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (16,000) in cell F8 of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period) record the SO2 concentration from the ENVIDAS software 5 minute average in cell L8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The SO2 100 ppm primary SRM should already be attached to the Environics 6103 (section 7.2 above), and the regulator should have already been purged (section

7.2). Set the timer for 30 minutes (initial equilibration for SO2 was done in Section 6.0, Day of Assay Zero and Span).

7.4.6 During the waiting time, write the diluent MFC settings (16,000) in cell F9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the SO2 concentration from the ENVIDAS software 5 minute average in cell L9 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 10 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary SO2 SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve an SO2 reading between 0.400-0.450 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 20 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (16,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the SO2 concentration from the ENVIDAS software 5 minute average in cell L10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder

regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows and SO2 analyzer readings should be entered in ranges F11..F14, and L11..L14, respectively for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range F20..F26, and analyzer results will be placed in cell range L20..L26.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range F32..F38, and analyzer results are reported in cell range L32..L48.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed Concentrations and Finalization of Assay Worksheet.

Note: This portion of the SOP will calculate the final concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it

into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

7.7.1 Scroll to cell R42 in the Assay Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.2 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.3 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.7.4 For challenge standard #1: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.5 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S70 → right click → paste special → values → OK.

7.7.6 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U94 → right click → paste special → values → OK.

7.7.7 For challenge standard #2: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.8 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V70 → right click → paste special → values → OK.

7.7.9 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X94 → right click → paste special → values → OK.

7.7.10 For challenge standard #3: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.11 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y70 → right click → paste special → values → OK.

7.7.12 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA94 → right click → paste special → values → OK.

7.7.13 **For challenge standard #4**: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.14 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB70 → right click → paste special → values → OK.

7.7.15 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD94 → right click → paste special → values → OK

7.7.16 **For challenge standard #5**: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.17 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE70 → right click → paste special → values → OK.

7.7.18 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG94 → right click → paste special → values → OK

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-SO2 workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step These are the various analytical steps taken to conduct this assay.

QA Requirement Quality Assurance requirements are derived from the EPA Protocol

Result These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.

Status A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a “warning” level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-SO2 workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

APPENDIX C:

WORKING INSTRUCTIONS

FOR

OXIDES OF NITROGEN ASSAYS

FOR THE

PROTOCOL GAS VERIFICATION PROGRAM

IN US EPA REGION 7

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Table of Contents

1.0 Introduction and Caveats

This procedure is designed for use with the Excel workbook **PGVP-NOx v3.1.xls.** When using and/or archiving the PGVP-NOx Workbook, save it according to the following convention:

MDW_AAPGVP_R2_2010_1_N_01

Where:

1. Work Sheet Identifier: MDW
2. Program Identifier: AAPGVP
3. Region : R2
4. Year: YYYY
5. Quarter: 1-4
6. Pollutant – (C=CO, S= SO2, N=NOX)
7. Batch/Run: 01 –XX

The file label above is an example of a MDW for the Protocol Gas Program, performed by Region 2 in 2010 in quarter 1, and is the first run for NOx data.

2.0 Assay Information Worksheet

The PGVP-NOx Workbook, Assay Information worksheet, contains 6 information blocks to be filled by the analyst. Below, each block is listed and any special requirements/comments are identified.

A. Laboratory Information The date field is shaded in green and is not filled out here. The date field is a pointer to the date of assay filled out in the Assay Worksheet, during the assay (Section 7.0). This date is used as the reference for checking the time limits on calibrations, leak checks, and all other expiration dates.

B. SRM Standards for Carbon Monoxide Assays The laboratory will have 2 SRM standards of differing concentration for each pollutant assayed. One SRM is the primary standard, and the second is designated as a check standard. This facilitates the leak check by dilution requirement of the Protocol.

C. Laboratory Flow Standards Enter the relevant information and calibration expiration dates.

D. Gas Dilution Calibrator Information The Calibrator Calibration Date and Notes fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Calibration Flow Cal worksheet. They should be left blank when filling out the rest of this form.

E. Ambient Air Analyzer Information The Date of Calibration, Slope, and Intercept fields are shaded in green. These fields are not filled out on this sheet, but are carried over from the Analyzer Cal worksheet. They should be left blank when filling out the rest of this form.

F. Carbon Monoxide Challenge Standards Under Test Fill out all the requested information in the fields provided.

After completing the Assay Information worksheet, print a copy and 1) tape/glue it into the PGVP laboratory logbook or 2) record all the data manually into the laboratory logbook.

3.0 Flow Calibration of Environics 6103: Procedure & Calibrator Flow Cal Worksheet

Note: The Environics 6103 must be calibrated within 2 weeks of any assay.

3.1 Calibration Procedure

The Environics 6103 calibration procedure is detailed in the Working Instructions for Carbon Monoxide Assays, and is not reproduced here. Current Environics 6103 flow calibration data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-NO/NOx) in order to use the current calibration. The procedure for copying this data is as follows:

3.1.1 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet, highlight cell range B3..K28.

3.1.2 Select edit from the menu bar → clear→ all.

3.1.3 Go to the PGVP-CO workbook, Calibrator Flow Cal worksheet, → highlight cell range B1..K26 → right click → copy.

3.1.4 Select the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

3.1.5 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet, delete all cells with data from row N50 and below.

3.1.6 Select the PGVP-CO workbook, Calibrator Flow Cal worksheet, highlight all cells with data commencing with cell N48 and below → right click →copy

3.1.7 In the PGVP-NO/NOx workbook, Calibrator Flow Cal worksheet → highlight cell N50 → right click → paste.

3.1.8 Close the PGVP-CO workbook that was used.

3.2 Select-a Cal Gas Assay Flow Selection Tool

The Select-a-Cal is a tool to help select the appropriate flow rates for use in gas assays to ensure that the flow rates selected will result in concentrations in the ranges desired. The analyst enters the gas to be assayed, the nominal concentration of the gas, and the diluent and pollutant MFC settings that are under consideration. Using the calibration slope and

intercept determined previously, a predicted flow for each MFC and final gas concentrations are calculated. The drop down menus in the user input columns default to the gases and MFC ranges that are used for PGVP in the flow calibration. Nevertheless, the user may enter any gas, concentration, and flow setting desired, thus overriding the drop down window defaults.

4.0 Thermo 42i NO/NOx Calibration Procedure & Analyzer Cal Worksheet

Note: The analyzer is set to a range of 0.500 ppm NO/NOx.

Note: The NO/NOx analyzer must be warmed up for a minimum of 3 hours prior to the start of analysis. Overnight sampling of zero air is recommended.

Note: The NO/NOx Procedure measures NO *and* NOx to account for NO impurities. Therefore, there are extra fields for NO and NOx data in the Assay Info, Analyzer Cal, Day of Assay Zero and Span, Assay Worksheet, QA, and Certificate worksheets in the PGVP-NOX workbook.

Note: Analyzer Calibration must be done within 2 weeks of any assay.

Note: The regulator for the pollutant gases should be installed the night before.

Note: Initial upscale points require 40 minutes for NO/NOx equilibration. Later points require a 20 minute equilibration time

Note: The procedure for setting flow rates for the Environics 6103 is described in the Working Instructions for Carbon Monoxide Assays, Section 3.2, will not be repeated here.

4.1 Required Materials

a. Thermo 42iC ambient air analyzer

b. Environics 6103 gas dilution calibrator

c. Clean zero air source capable of delivering a pressure of 30 psig

d. Glass manifold for connecting calibrator, analyzers, and exhaust line

e. 100 ppm NO/NOx SRM and CGA 660 pressure regulator

f. Teflon tubing, Swagelok fittings, and wrenches for connections

g. Computer with ENVIDAS data logging software, EXCEL for Windows, PGVP-NOx workbook, and cables/interfaces for computer hookup

h. Laboratory timer, laboratory logbook, pens

4.2 Connection of Environics 6103 to NO/NOx Assay System

4.2.1 Move the Environics 6103 calibrator to its dedicated space on in the ambient air analyzer rack for the PGVP assay.

4.2.2 Connect the zero air supply to the Port 1 inlet on the back of the Environics 6103 and turn the on the Environics 6103. Set the zero air supply regulator to 30 psi.

4.2.3 Connect the ½" output line from the Environics 6103 to the glass NO/NOx manifold. The NO/NOx analyzers are by default plumbed to the glass manifold via ¼" Teflon lines. The exhaust of the manifold is vented via a ½" line to the laboratory venting system.

4.2.4 Set the Environics 6103 calibrator to deliver 16.0 L/min of zero gas to the NO/NOx manifold. Let the NO/NOx analyzers sample the zero air flow overnight.

4.2.5 Turn on the Thermo 42i NO/NOx analyzer(s).

4.2.6 Install the CGA 660 stainless steel regulator on the 100 ppm NO/NOx SRM cylinder. The cylinder should be charged overnight according to the following procedure.

a. Turn the delivery valve of the pressure regulator to the closed position.

b. Turn the cylinder valve of the NO/NOx SRM open. Observe, and record in the laboratory logbook, the cylinder pressure reading on the pressure regulator.

c. Set the pressure regulator delivery pressure for 30 psi.

d. Close the cylinder valve. The pressure regulator will remain under pressure.

e. Check to verify that the SRM cylinder valve is closed.

4.2.7 Purge the NO/NOx SRM regulator according to the following procedure:

a. Attach a ¼" delivery line to the pressure regulator connected to the NO/NOx SRM.

b. Vent the regulator by opening the regulator output valve (the cylinder should be closed as per step 4.1.6)

c. Close the regulator output valve.

d. Open the cylinder valve, pressurizing the regulator.

e. Close the cylinder valve.

f. Vent the regulator as per step b above.

g. Repeat the pressurizing/venting steps in steps d through f, 2 more times.

4.2.8 Connect the output of the NO/NOx SRM to Port 2 of the Environics 6103.

4.2.9 Open the NO/NOx SRM cylinder valve and adjust the delivery pressure on the regulator to 30 psi.

4.3 Data Logging Software (ENVIDAS) Startup

To be added later

4.4 Calibration of the Thermo 42i NO/NOx Analyzer

4.4.1 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/minutes.

4.4.2 Allow the Thermo 42i 20 minutes to sample the Environics 6103 calibrator output.

4.4.3 During the waiting time for sample equilibration, push the **MENU** button (it is the 2nd button down, on the left hand side of the analyzer and it has a page icon printed on it), and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER** (the enter button has a return icon printed on it and it is centered between the 4 directional arrow buttons used to move the cursor)**.** Record the **NO BKG, NOx BKG, NO COEF,** and **NOX COEF** displayed on the Thermo 42i LCD in the laboratory logbook under the heading Thermo 42i Pre Calibration Background & NO/NOx Coefficient Readings. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 42i analyzer, and designated by a right pointing solid triangle icon).

4.4.4 After a steady trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** A new screen will appear on the LCD with the cursor pointing to **CAL NO BACKGROUND**. Press **ENTER.** The Thermo 42i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET NO TO ZERO.** Press **ENTER.** After setting the NO zero, push the **MENU** button on the Thermo 42i front panel. This will bring you back to the previous screen. Push the down arrow on the front panel to bring cursor in front of the **CAL NOX BACKGROUND** line, and push **ENTER**. The Thermo 42i display will show a new screen, with the bottom line of the display showing the **ENTER** icon and **SET NOX TO ZERO.** Press **ENTER**. After setting the NOx zero, push the **RUN** button to resume at the main display screen.

4.4.5 Set the Environics 6103 pollutant MFC to 78.0 cc/min. The diluent MFC should remain at 16.0 L/min.

4.4.6 Allow the Thermo 42i to sample the Environics 6103 output for 40 minutes.

4.4.7 During this waiting period, open the Excel PGVP-NO/NOx Workbook that will be used for this batch of NO/NOx assays. The Assay Information worksheet should have already been filled out as outlined in Section 2.0 above.

4.4.8 Go to the Analyzer Cal worksheet and enter 16000 for the High MFC Device setting in cells B14 (NO portion of analyzer calibration) and B23 (NOX portion of analyzer calibration). The delivered concentration will be displayed in cell F14 (for NO) and Cell F23 (for NOx), for the current conditions (Environics 6103 set for 16.0 L/min diluent and 78.0 cc/min pollutant gas using the 100 ppm NO/NOx SRM).
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4.4.9 After the 40 minute waiting period and a steady data trace is observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period), push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION** line. Press **ENTER.** The Thermo 42i display will show a new window with the cursor defaulting to the **CAL NO BACKGROUND** line. Using the front panel arrow keys, place the cursor in front of the **CAL NO COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.10 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered NO/NOx concentration specified in cell F14 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **MENU** button to get to the previous screen on the Thermo 42i.

4.4.11 Using the front panel arrow keys, place the cursor in front of the **CAL NOX COEFFICIENT** line and press **ENTER.** A new window will be displayed showing the current analyzer NOx reading and span concentration. The cursor will default to the last decimal place on the line reading **SPAN CONC: 0000.XXX**

4.4.12 Using the arrow buttons on the front panel, increment (or decrement if that is the case) the value displayed in the **SET TO 000XX.X00?** to equal the delivered NO/NOx concentration specified in cell F23 of the Analyzer Cal worksheet. Press **ENTER** to accept this value. The analyzer reading will be the entered value. Push the **MENU** button to get to the main analyzer screen on the Thermo 42i.

4.4.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min and wait 15 minutes for equilibration.

4.4.14 During the waiting time for sample equilibration, push the **MENU** button, and using the arrow keys on the front panel align the cursor to point to the **CALIBRATION FACTORS** line. Press **ENTER.** Record the **NO BKG, NOx BKG, NO COEF,** and **NOX COEF** displayed on the Thermo 42i LCD in the laboratory logbook under the heading Thermo 42i Post Calibration Background & NO/NOx Coefficient Readings. After taking the readings, push the **RUN** button (top button on the left hand side of the Thermo 42i analyzer, and designated by a right pointing solid triangle icon).

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4.4.15 After a steady trace is observed , record the 5 minute average provided by the ENVIDAS data system and record it in the laboratory logbook under the heading Post Calibration Zero.

4.5 Thermo 42i Calibration for the NO/NOx Assay using the Analyzer Cal Worksheet

Note: All non shaded cells have their values automatically entered into the Analyzer Cal worksheet from the Assay Info and Calibrator Flow Cal worksheets.

4.5.1 In the Analyzer Cal worksheet, enter the current date in cell B5, and include any relevant notes in cell J5. These cells are shaded in yellow.

4.5.2 Set the Environics pollutant MFC to 78.0 cc/min. Set the timer for 20 minutes.

4.5.3 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G14 (analyzer response), and the NOX concentration in cell G23 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.4 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

4.5.5 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G15, and the NOX concentration in cell G24 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.6 Set the Environics pollutant MFC to 60.0 cc/min. Set the timer for 20 minutes.

4.5.7 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G16, and the NOX concentration in cell G25 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.8 Set the Environics pollutant MFC to 50.0 cc/min. Set the timer for 20 minutes.

4.5.9 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G17, and the NOX concentration in cell G26 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.10 Set the Environics pollutant MFC to 40.0 cc/min. Set the timer for 20 minutes.

4.5.11 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G18, and the NOX concentration in cell G27 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.5.12 Set the Environics pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

4.5.13 After the timer has beeped, and when a steady trace is observed, record the 5 minute average NO concentration from the ENVIDAS software in cell G19, and the NOX concentration in cell G28 of the Analyzer Cal worksheet. Enter this concentration, and the current Environics MFC settings, into the laboratory logbook.

4.6 Determining the Analyzer Estimate of Uncertainty

Note: The estimate of uncertainty is a parameter that determines the range of concentrations where an analyzer is sufficiently well characterized for assay use. This value must be 1.00% or less to be considered well characterized.

Note: The analyzer uncertainty estimate must be calculated separately for the NO and NOx components.

4.6.1 In the Analyzer Cal worksheet, collect the delivered NO concentration and analyzer response: highlight cells F14..G19 → right click → copy.

4.6.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer calibration data for NO into this worksheet.

4.6.3 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.4 Select cell F14 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.5 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I14 → right click → paste special → values → OK.

4.6.6 Repeat steps 4.6.4 and 4.6.5 for each cell in the range F15..F18 (one cell at a time), recording the results in cells I15..I18, respectively.

4.6.7 In the Analyzer Cal worksheet, collect the delivered NOx concentration and analyzer response: highlight cells F23..G28 → right click → copy.

4.6.8 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer calibration data for NOx into this worksheet.

4.6.9 In the Measurement Data worksheet, select cell D166, and enter the number 3 (r=3). This is the number of challenge, zero, and SRM test sets that will be run during the assay.

4.6.10 Select cell F23 in the Analyzer Cal Worksheet (analyzer response) → right click → copy. Open the Measurement Data worksheet → select cell D164 (Concentration =)→ right click → paste special → values →OK.

4.6.11 Select cell F185 in the Measurement Data worksheet (95% uncertainty in prediction)→ right click → copy. Go to the Analyzer Cal worksheet cell I23 → right click → paste special → values → OK.

4.6.12 Repeat steps 4.6.10 and 4.6.11 for each cell in the range F24..F27 (one cell at a time), recording the results in cells I24..I27, respectively.

5.0 Environics 6103 Dilution Leak Check Procedure & Calibrator Dilution Check Worksheet

Note: The dilution check is a requirement of the EPA Protocol when using a dilution device (G2 method). The method requires assay of 2 SRMs of the same compound with different concentrations

Note: The dilution check must be completed within 2 weeks of any assay.

Note: The dilution check must be completed with an analyzer that has been calibrated within 2 weeks of any assay

5.1 Dilution Check Procedure

The Environics 6103 dilution check procedure is detailed in the Working Instructions for Carbon Monoxide Assays, Section 5.0, and is not reproduced here. Current Environics 6103 dilution check data are collected, calculated, and reported using the PGVP-CO workbook. The data must be copied to this workbook (PGVP-NO/NOx) in order to use the current calibration. The procedure for copying this data is as follows:

5.1.1 In the PGVP-NO/NOx workbook, Calibrator Dilution Check worksheet, highlight cell range B3..K35.

5.1.2 Select edit from the menu bar → clear→ all.

5.1.3 Go to the PGVP-CO workbook, Calibrator Dilution Check worksheet, → highlight cell range B2..K34 → right click → copy.

5.1.4 Select the PGVP-NO/NOx workbook, Calibrator Dilution Check worksheet→ highlight cell B3 → right click → paste special → values → OK → right click → paste special→ formats → OK.

5.1.5 Close the PGVP-CO workbook that was used.

6.0 Day of Assay Zero, Span, and Precision Procedure and Day of Assay Zero & Span Worksheet

Note: Standard Procedure in Region 2 is to calibrate the ambient analyzer used for assay prior to the day of assay due the length of time calibrations and assays take. As required by the EPA Protocol, the analyzer used for assay must be zero and span checked on the day of analysis to ensure that any instrument drift is accounted for.

6.1 Required Materials

The required materials are the same as for Section 4.0 above.

6.2 Day of Assay Zero, Span, and Precision Procedure and Worksheet

6.2.1 Open the PGVP-NOx workbook for the current assay and open the Day of Assay Zero and Span worksheet.

Note: All non shaded cells have their values automatically entered into the Day of Assay Zero and Span worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

6.2.2. Ensure that the ENVIDAS software is logging the Thermo 42i output data stream.

6.2.3 Equilibrate the regulator on the Primary NO/NOx SRM overnight following the procedure given in Section 4.2.6.

6.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

6.2.5 The Thermo 42i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the zero, span, and precision tests.

6.2.6 Purge the regulator of the Primary NO/NOx SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

6.2.7 Connect the Environics 6103 to the NO/NOx glass delivery manifold.

6.2.8 Set the Environics 6103 diluent MFC to 16.0 L/min, and the pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.9 During the wait time, enter 16,000 in the High MFC Device Setting column in cells D18..D23 and D41..D46.

6.2.10 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J18 for NO and J41 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.11 Set the Environics 6103 pollutant MFC to 70.0 cc/min. Set the timer for 40 minutes.

6.2.12 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J19 for NO and J42 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.13 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.14 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J20 for NO and J43 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.15 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.16 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J21 for NO and J44 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.17 Set the Environics 6103 pollutant MFC to 0.0 cc/min. Set the timer for 15 minutes.

6.2.18 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J22 for NO and J45 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.2.19 Set the Environics pollutant MFC to 70.0 cc/min. Set the timer for 20 minutes.

6.2.20 After the timer has beeped, and a steady trace has been achieved, record the NO and NOx concentrations from the ENVIDAS software 5 minute average in cell J23 for NO and J46 for NOx of the Day of Assay Zero and Span worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

6.3 Day of Assay Zero and Span Worksheet Finalization and Evaluation for NO

After the runs are completed, data will be evaluated using the Measurement Data worksheet in the PGVP-NOx Workbook. This worksheet is the original worksheet from the EPA Protocol method, Appendix A. This spreadsheet is treated as a black box, in that the calculations derived from its calculations are accepted and the mechanics used to derive them are taken as accurate. Therefore calculations conducted using this worksheet are not presented here. The procedure for inputting data to and from this worksheet are presented below.

Note: This assay is for both NO and NOx. These two pollutants have different calibrations. In order to determine the instrument drift via the analysis of day of assay zero and span, the appropriate analyzer calibration data must first be loaded into the Measurement Data worksheet. This is done, for NO, in steps 6.3.1 - 6.3.2 below.

6.3.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F14..G19 → right click → copy. This is done to collect the NO calibration data originally obtained in Section 4.0.

6.3.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer NO calibration data into this worksheet.

6.3.3 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J18, J20, and J22 → right click → copy.

6.3.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.3.5 Select the Day of Assay Zero and Span worksheet, collect the predicted NO concentration: press escape → left click on cell H19 → control-left click on H21, and H23 → right click → copy.

6.3.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NO response: press Escape → left click on cell J19 → control-left click on J21, and J23 → right click → copy.

6.3.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.3.9 In the Measurement Data worksheet, select cell range D249..G253 → copy.

6.3.10 Select the Day of Assay Zero and Span worksheet → select cell D27 → right click → paste special → values → OK.

6.3.11 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D29 and D31, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.3.12 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F29 and F31, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4 Day of Assay Zero and Span Worksheet Finalization and Evaluation for NOx

Note: This assay is for both NO and NOx. These two pollutants have different calibrations. In order to determine the instrument drift via the analysis of day of assay zero and span, the appropriate analyzer calibration data must first be loaded into the Measurement Data worksheet. This is done, for NOx, in steps 6.4.1 - 6.4.2 below.

6.4.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F23..G28 → right click → copy. This is done to collect the NOx calibration data originally obtained in Section 4.0.

6.4.2 Open the Measurement Data worksheet in the current Excel workbook →. Select cell C11 → right click → paste special → values → OK. This enters the analyzer NOx calibration data into this worksheet.

6.4.3 In the Day of Assay Zero and Span worksheet collect the response to zero gas: control-left click on cells J41, J43, and J45 → right click → copy.

6.4.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

6.4.5 Select the Day of Assay Zero and Span worksheet collect the predicted NOx concentration: press escape → left click on cell H42 → control-left click on H44, and H46 → right click → copy.

6.4.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.4.7 Select the Day of Assay Zero and Span worksheet collect the analyzer NOx response: press Escape → left click on cell J42 → control-left click on J44, and J46 → right click → copy.

6.4.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

6.4.9 In the Measurement Data worksheet, select cell range D249..G253 → right click → copy.

6.4.10 Select the Day of Assay Zero and Span worksheet → select cell D50 → right click → paste special → values → OK.

6.4.11 In the Day of Assay Zero and Span worksheet, the zero gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells D52 and D54, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4.12 In the Day of Assay Zero and Span worksheet, the span gas results for standard error (a measure of precision) and relative difference (a measure of accuracy) are indicated in cells F52 and F54, respectively. These results are copied directly from the Measurement Data worksheet in step 6.3.9 above.

6.4.13 If acceptable results are obtained for the parameters in 6.3.9 and 6.3.10 and 6.4.9 and 6.4.10 (…is okay), save all data from the ENVIDAS data logging program in the PGVP workbook, and proceed to the Assay Worksheet and Section 7 of these instructions.

7.0 NO/NOx Assay Procedure and Assay Worksheet

The Assay procedure consists of 3 test runs consisting of zero, Primary NO/NOx SRM Standard, and all candidate standards. The worksheet can accommodate up to 5 challenge cylinders at a time.

7.1 Required Materials

The required materials are the same as for Section 4.0 above, with the addition of challenge cylinders.

7.2 Assay and Assay Worksheet

7.2.1 Open the PGVP-NOx workbook for the current assay and open the Assay Worksheet.

Note: All calculations of flow and predicted concentrations, as well as cylinder information have their values automatically entered into the Assay Worksheet from the Assay Info, Calibrator Flow Cal, and Analyzer Cal worksheets.

7.2.2. Ensure that the ENVIDAS software is logging the Thermo 42i output data stream.

7.2.3 Equilibrate regulators to be used for the assay overnight following the procedure given in Section 4.2.6.

7.2.4 The Environics 6103 should be warmed up for at least an hour prior to performing this procedure.

7.2.5 The Thermo 42i must be warmed up for at least 3 hours (overnight preferable) prior to conducting the assay.

7.2.6 Purge the regulator of the Primary NO/NOx SRM as per Section 4.2.7, and connect it to Port 2 of the Environics 6103. Set the pressure regulator to deliver 30 psig.

7.2.7 Connect the Environics 6103 to the NO/NOx glass delivery manifold.

7.3 Selection of Flow Rates for Challenge Standards

It is essential that the analysis of each standard be at a concentration > 80% of the upper range limit (URL) of the Thermo 42i NO/NOx analyzer, because this where the analyzer is most accurate and precise. For this assay, the range of the analyzer will be 0-0.500 ppm (0-500 ppb). With challenge standard cylinder concentrations of 25 – 100 ppm, the 80% URL requirement is achieved by adjusting the Environics 6103 diluent MFC flow in a range of 4.0 – 16.0 L/min. The table below gives examples of cylinder concentrations, and the diluent MFC flow rates used, to achieve the 80% URL requirement. For cylinders at concentrations not shown below, the Select-A-Cal tool, referred to in Section 3.8, can be used to determine the diluent MFC flow rate required. The pollutant MFC flow rates should remain constant at 70.0 cc/min, in order to achieve the highest level of assay accuracy.

Diluent MFC Flow Rate Selection Chart					
Gas Type	Candidate cylinder concentration (ppm)	SRM Concentration to be used (in ppm)	The diluent mass flow controller is set to: (in L/min)	The Diluent Mass Flow Controller is set to: (in cc/min)	The Concentration at the analyzer will be (in ppm):
NO or NOx	100	100	16.0	70	0.433
	50	100	8.0	70	0.432
	25	100	4.0	70	0.430

7.4 Assay Procedure Test Set 1

7.4.1 In cell C3 (yellow shaded) of the Assay Worksheet fill in the day of the assay.

7.4.2 Set the Environics 6103 diluent MFC to 16.0 L/min, and the diluent MFC to 0.0 cc/min. Set the timer to15 minutes.

7.4.3 During the waiting time, write the diluent MFC settings (16,000) in cell G8 and of the Assay Worksheet.

7.4.4 After the timer has beeped, and a stable trace observed (defined as a reading not varying by more than 0.002 ppm over a 5 minute period) record the NO concentration from the ENVIDAS software 5 minute average in cell M8, and the NOx concentration in cell N8 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.5 Set the Environics 6103 pollutant MFC to 70.0 cc/min. The diluent MFC setting is not varied. The NO/NOx 100 ppm primary SRM should already be attached to the

Environics 6103 (section 7.2 above), and the regulator should have already been purged (section 7.2). Set the timer for 40 minutes.

7.4.6 During the waiting time, write the diluent MFC settings (16,000) in cell G9 of the Assay Worksheet.

7.4.7 After the timer has beeped, and a stable trace observed record the NO/NOx concentration from the ENVIDAS software 5 minute average in cell M9, and the NOx concentration in cell N9 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.8 Set the Environics 6103 pollutant MFC to 0.0 cc/min and set the timer for 15 minutes. This is to flush the system with zero gas, although a data point will not be taken for this step. This flush step is taken after each cylinder standard (challenge and primary) is assayed.

7.4.9 During the waiting time:

a. Close the regulator and cylinder valves of the primary NO/NOx SRM
b. Disconnect the cylinder from Port 2 of the Environics 6103.
c. Purge the regulator of challenge cylinder #1.
d. Connect challenge cylinder #1 to port 2 of the Environics 6103.

Note: The challenge cylinders in the 1st test set are run in the order they were entered in the Assay Information Worksheet. The Assay Worksheet has already entered the cylinders to be assayed and the order they should be run.

7.4.10 After the timer has beeped, set the Environics 6103 diluent MFC to 70.0 cc/min.

7.4.11 Set the Environics 6103 diluent MFC to the values appropriate to achieve a NO/NOx analyze reading between 0.400-0.450 ppm. Use either the table listed in Section 7.3 or the Select-A-Cal (see Section 3.8), to determine the proper flow. The diluent MFC flow must be in 4.0 – 16.0 L/min range.

7.4.12 Set the timer for 15 minutes.

7.4.13 During the waiting time, write the diluent MFC settings (16,000) in cell F10 of the Assay Worksheet.

7.4.14 After the timer has beeped, and a stable trace observed, record the NO/NOx concentration from the ENVIDAS software 5 minute average in cell M10, and the NOx concentration in cell N10 of the Assay Worksheet. Record the Environics MFC settings and analyzer output in the laboratory logbook.

7.4.15 Repeat steps 7.4.8 - 7.4.14 for each of the challenge cylinders in turn, making sure to close the previous cylinder's regulator and cylinder valve, and to purge each cylinder

regulator prior to first use. If a regulator must be taken from one cylinder to be put on another, the regulator must be purged prior to use. Data for MFC pollutant flows NO, and NOx analyzer readings should be entered in ranges G11..G14, M11..M14, and N11..N14 \, respectively, for each challenge standard in turn.

Note: It is critical that the proper diluent MFC setting is chosen for each challenge cylinder, and entered correctly in the worksheet. Double check that the proper flow settings are used, entered, and logged.

7.5 Assay Procedure Test Set 2

Assay Procedure test set 2 is identical to test set 1, with the exception that the order that cylinders are assayed has been switched. The Analysis Worksheet has automatically reordered the cylinders. Follow the procedure outlined in steps 7.4.8 – 7.4.15 with the following exceptions:

a. Cylinder MFC diluent flows will be recorded in range G20..G26, and analyzer NO and NOx results will be placed in cell range M20..M26 and N20..N26. respectively.

b. Cylinder regulators do not require repurging if they have not been removed from the cylinder since their initial purge during test set 1.

c. Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.6 Assay Procedure Test Set 3

Follow the procedure and caveats listed for test set 2 during test set 3. In test set 3, diluent MFC flows are reported in cell range G32..G38, and analyzer NO and NOx results are reported in cell range M32..M38 and N32..N38, respectively.

Be vigilant about which cylinder is being analyzed. It is very easy to get confused with all of the cylinder switching going on. Verify the correct cylinder is being analyzed before it being assayed and again on completion of its test run. Double check that the flow rates used for the diluent MFC are correct.

7.7 Determination of Assayed NO Concentrations and Finalization of NO Portion of the Assay Worksheet.

Note: This portion of the SOP will calculate the final NO concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

Note: This assay includes both NO and NOx results. Section 7.7 pertains to the NO portion of the assay, and both the analyzer calibration data for NO, as well as the day of assay zero and span results must be re-entered into the Measurement Data worksheet. In Section 7.8, the same process will be applied to NOx results.

7.7.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F14..G19 → right click → copy. This is done to collect the NO calibration data originally obtained in Section 4.0.

7.7.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer NO calibration data into this worksheet.

7.7.3 In the Day of Assay Zero and Span worksheet, collect the response to zero gas: control-left click on cells J18, J20, and J22 → right click → copy.

7.7.4 Select cell C233 in the Measurement Data worksheet, → right click → paste special → values → OK.

7.7.5 Select the Day of Assay Zero and Span worksheet, collect the predicted NO concentration: press escape → left click on cell H19 → control-left click on H21, and H23 → right click → copy.

7.7.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.7.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NO response: press Escape → left click on cells J19 → control-left click on J21, and J23 → right click → copy.

7.7.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.7.9 Scroll to cell R42 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.7.10 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S48..T50 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.7.11 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U48..V50 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.7.12 **For challenge standard #1**: In the Assay Worksheet, highlight cells W48..W50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.13 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S75 → right click → paste special → values → OK.

7.7.14 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U99 → right click → paste special → values → OK.

7.7.15 **For challenge standard #2**: In the Assay Worksheet, highlight cells X48..X50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.16 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V75 → right click → paste special → values → OK.

7.7.17 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X99 → right click → paste special → values → OK.

7.7.18 **For challenge standard #3**: In the Assay Worksheet, highlight cells Y48..Y50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.19 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y75 → right click → paste special → values → OK.

7.7.20 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA99 → right click → paste special → values → OK.

7.7.21 For challenge standard #4: In the Assay Worksheet, highlight cells Z48..Z50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.22 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB75 → right click → paste special → values → OK.

7.7.23 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD99 → right click → paste special → values → OK

7.7.24 For challenge standard #5: In the Assay Worksheet, highlight cells AA48..AA50 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.7.25 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE75 → right click → paste special → values → OK.

7.7.26 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG99 → right click → paste special → values → OK.

7.8 Determination of Assayed NOx Concentrations and Finalization of NOx Portion of the Assay Worksheet.

Note: This portion of the SOP will calculate the final NOx concentrations of the challenge cylinders. It involves copying data from the Assay Worksheet, pasting it into the Measurement Data worksheet to get the relevant calculations, followed by pasting the results back to the Assay Worksheet.

Note: This assay includes both NO and NOx results. Section 7.8 pertains to the NOx portion of the assay, and both the analyzer calibration data for NOx, as well as the day of assay zero and span results must be re-entered into the Measurement Data worksheet.

7.8.1 In the PGVP-NOx workbook, Analyzer Cal worksheet, highlight cells F23..G28 → right click → copy. This is done to collect the NOx calibration data originally obtained in Section 4.0.

7.8.2 Open the Measurement Data worksheet in the current Excel workbook → Select cell C11 → right click → paste special → values → OK. This enters the analyzer NOx calibration data into this worksheet.

7.8.3 In the Day of Assay Zero and Span worksheet collect the response to zero gas: control-left click on cells J41, J43, and J45 → right click → copy.

7.8.4 Select cell C233 in the Measurement Data worksheet → right click → paste special → values → OK.

7.8.5 Select the Day of Assay Zero and Span worksheet collect the predicted NOx concentration: press escape → left click on cells H42 → control-left click on H44, and H46 → right click → copy.

7.8.6 Select cell E233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.8.7 Select the Day of Assay Zero and Span worksheet and collect the analyzer NOx response: press Escape → left click on cells J42 → control-left click on J44, and J46 → right click → copy.

7.8.8 Select cell F233 in the Measurement Data worksheet→ right click → paste special → values → OK.

7.8.9 Scroll to cell R102 in the Analysis Worksheet. This will show the results for each test set, segregated by cylinder.

7.8.10 Copy the zero gas calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells S108..T110 → right click → copy → go to the Measurement Data worksheet, cell B276 → right click → paste special → values → OK.

7.8.11 Copy the primary SRM calculated concentrations and instrument response as follows: In the Assay Worksheet, highlight cells U108..V110 → right click → copy → go to the Measurement Data worksheet, cell B279 → right click → paste special → values → OK.

7.8.12 **For challenge standard #1**: In the Assay Worksheet, highlight cells W108..W110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.13 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell S135 → right click → paste special → values → OK.

7.8.14 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell U159 → right click → paste special → values → OK.

7.8.15 For challenge standard #2: In the Assay Worksheet, highlight cells X108..X110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.16 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell V135 → right click → paste special → values → OK.

7.8.17 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell X159 → right click → paste special → values → OK.

7.8.18 For challenge standard #3: In the Assay Worksheet, highlight cells Y108..Y110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.19 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell Y135 → right click → paste special → values → OK.

7.8.20 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AA159 → right click → paste special → values → OK.

7.8.21 For challenge standard #4: In the Assay Worksheet, highlight cells Z108..Z110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.22 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AB135 → right click → paste special → values → OK.

7.8.23 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AD159 → right click → paste special → values → OK

7.8.24 For challenge standard #5: In the Assay Worksheet, highlight cells AA108..AA110 → right click → copy → go to the Measurement Data worksheet, cell H276 → right click → paste special → Values → OK.

7.8.25 Transfer calculations from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cells G276..I295 → right click → copy → go to the Assay Worksheet, highlight Cell AE135 → right click → paste special → values → OK.

7.8.26 Transfer the 95% uncertainty of analysis from the Measurement Data worksheet as follows: In the Measurement Data worksheet, highlight cell B305 → right click → copy → go to the Assay Worksheet → highlight cell AG159 → right click → paste special → values → OK.

8.0 QA (Quality Assurance) Worksheet

The QA Worksheet contains no direct user input data. All information displayed is from pointers from the other worksheets in the PGVP-NOx workbook. There are 4 columns; analytical step, QA requirement, Result, and Status. Below is an explanation/notes of these columns:

Analytical Step These are the various analytical steps taken to conduct this assay.

QA Requirement Quality Assurance requirements are derived from the EPA Protocol

Result These are the results for each QA requirement. By clicking on a cell in this column, the source of the original data is shown in the EXCEL formula bar at the top of the page.

Status A logical test is conducted on the result to determine if the QA requirement was met. The logical test can be seen in the EXCEL formula bar when a cell in this column is highlighted. Conditional formatting has been added to this column, such that an acceptable status returns a green background, an unacceptable result returns a red background, and for challenge cylinders only, a "warning" level returns a yellow background.

9.0 Certificates Worksheet

The Certificates worksheet is filled out automatically by the PGVP-NOx workbook, and no direct user input is required for this sheet. Nevertheless, verify that the certificate data is correct, by the comparing the certificate value with the raw data components in the Assay Worksheet and Assay Information worksheet.

APPENDIX D:

SCREEN SHOTS

FROM THE

PGVP-CO WORKBOOK

PGVP Carbon Monoxide Assay Information

EPA Region 2

Laboratory & Location:	EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ	Date of PGVP Assay:	11-Feb-10
Verification Conducted By:	Avi Teitz/Mustafa Mustafa	Laboratory Manager:	Avi Teitz/Mustafa Mustafa

SRM Standards for Carbon Monoxide Assays

Type of Standard	Manufacturer	SRM #	Cylinder Serial #	Concentration (ppm)	Cylinder Pressure During Assay	Expiration Date	Notes
Primary Std.	Scott	SRM 2639a	ALM1234567	9982	1200	31-Mar-11	
Check Std.	Praxair	SRM 2638a	FF1234567	5000	900	31-Mar-11	

Laboratory Flow Standards

Manufacturer	Model #	Serial #	Certification Date	Range	Notes
BIOS	ML-800 Cell 44	104396	5-May-10	0.5 - 30L/min	High Flow Cell
BIOS	ML-800 Cell 10	106328	5-May-10	5-300 cc/min	Low Flow Cell
BIOS	ML-800 Base	105428	5-May-10	N/A	Base unit w/ Temp & Pressure

Gas Dilution Calibrator Information

Manufacturer	Model #	Serial #	Calibrator Calibration Date	Notes
Environics	6103	4501	9-Feb-10	

CO Analyzer Information

Date of Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Slope	Intercept	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	1.00377	0.0663	

Carbon Monoxide Challenge Standards Under Test

Vendor	Cylinder Serial Number	Vendor Certified Concentration (ppm)	Balance Gas	Vendor Expiration Date	Date Received	Cylinder Pressure Received (psig)	Cylinder Pressure After Assay (psig)	Notes
Scott-Marrin	B12345678	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1800	1780	
Scott	C98765432	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1900	1880	
Praxair	D12345678	5000.00	Nitrogen	1-Jan-12	1-Dec-09	1850	1825	
BOC	E98765432	10000.00	Nitrogen	1-Jan-12	1-Dec-09	2000	1980	
Joe Blow	F12345678	2500.00	Nitrogen	1-Jan-12	1-Dec-09	1750	1725	

Calibrator Flow Calibration

Calibrator Information

Calibration Date	Manufacturer	Model #	Serial #	Notes
9-Feb-10	Environics	6103	4501	

Flow Standard Information

Manufacturer	Model #	Serial #	Annual Certification Date	Range	Notes
BIOS	ML-800 Cell 44	104396	5-May-10	0.5 - 30L/min	High Flow Cell
BIOS	ML-800 Cell 10	106328	5-May-10	5-300 cc/min	Low Flow Cell
BIOS	ML-800 Base	105428	5-May-10	N/A	Base unit w / Temp & Pressure

Flow Calibration

February 9, 2010

Zero Gas Mass Flow Controller					Pollutant Gas Mass Flow Controller				
MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction	MFC Setting (cc/min)	MFC Reading (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Curve Predicted	% error in curve prediction
16000	16010	15918	15913	-0.03%	78	78.10	77.16	77.11	-0.07%
12000	12008	11923	11926	0.02%	70	70.00	69.17	69.19	0.03%
8000	8006	7931	7939	0.11%	60	59.90	59.23	59.29	0.10%
6000	6019	5946	5946	-0.01%	50	49.90	49.38	49.39	0.02%
4000	4008	3958	3952	-0.15%	40	40.10	39.54	39.49	-0.10%
Slope		0.996744085	Slope of Calibrated MFC	0.999998504	Slope		0.989796423	Slope of Calibrated MFC	0.999990601
Intercept		-34.85673835	Intercept of Calibrated MFC	0.013668974	Intercept		-0.097130622	Intercept of Calibrated MFC	0.000553546

Select-a-Cal

Calibration Flow Selection Tool

February 9, 2010

Pollutant	Nominal Pollutant Concentration (ppm)	Zero MFC Setting (cc/min)	Zero MFC Predicted Flow (cc/min)	Pollutant MFC Setting (cc/min)	Pollutant MFC Predicted Flow (cc/min)	Predicted Concentration Delivered (ppm)
CO	10000	16000	15913.0	78	77.11	48.222
				70	69.19	43.291
				60	59.29	37.121
				50	49.39	30.943
				40	39.49	24.758

CO Analyzer Calibration

CO Analyzer Information

Date of Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

Delivered CO Concentration and Analyzer Response

High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Delivered CO Concentration (ppm)	Analyzer Response (ppm)	% Difference	Estimate of Uncertainty @ Each Calbration Point (Step 4 of prot97aa.xls spreadsheet)	Analyzer Calibration Curve Parameters	
16000	15913.0	78	77.11	**48.14**	**48.40**	0.55	**0.60%**	slope	1.003775
		70	69.19	**43.21**	**43.50**	0.66	**0.62%**		
		60	59.29	**37.06**	**37.20**	0.39	**0.67%**		
		50	49.39	**30.89**	**31.10**	0.69	**0.79%**	intercept	0.0662707
		40	39.49	**24.71**	**24.80**	0.35	**1.00%**		
		0	0.00	**0.00**	**0.10**				

Dilution Calibrator Leak Check

Calibrator Information

Date of Dilution Check	Calibration Date	Manufacturer	Model #	Serial #	Notes
11-Feb-10	9-Feb-10	Environics	6103	4501	

CO Analyzer Information

Date of Analyzer Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO Primary SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

CO Check SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2638a	CO	Praxair	5000.0	FF1234567	900	31-Mar-11

Dilution Check w/ CO Analyzer

Gas Type	Cylinder Concentrations	High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Predicted Calibrator Delivered Concentration	Predicted Analyzer Response	Actual Analyzer Response	Percent Difference
Primary SRM	9982	16000	15913.0	70	69.19	43.21	43.44	43.2	-0.56
Zero Gas	0	16000	15913.0	0	0.00	0.00	0.07	0.1	
Check SRM	5000	8000	7939.1	70	69.19	43.20	43.43	43.3	-0.29
Zero Gas	0	8000	7939.1	0	0.00	0.00	0.07	0.0	
Check SRM	5000	8000	7939.1	70	69.19	43.20	43.43	43.4	-0.06
Zero Gas	0	8000	7939.1	0	0.00	0.00	0.07	0.1	
Check SRM	5000	8000	7939.1	70	69.19	43.20	43.43	43.3	-0.29
Zero Gas	0	8000	7939.1	0	0.00	0.00	0.07	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	43.21	43.44	43.2	-0.56
					Average Check SRM Response =			43.3	

Relative % Difference	-0.217%

Relative % Difference must be less than 1% to qualify the calibrator for use in assays.

Day of Assay Carbon Monoxide Zero and Span Check

CO Analyzer Information

Date of Analyzer Calibration	Analyzer	Manufacturer	Model #	Serial #	Range	Notes
9-Feb-10	CO	Thermo	48C	48-29388-234	0-50 ppm	

CO Primary SRM Information

SRM #	Pollutant	Manufacturer	Certified Concentration (in ppm)	Cylinder Serial #	Cylinder Pressure (psig)	Expiration Date
SRM 2639a	CO	Scott	9982.3	ALM1234567	1200	31-Mar-11

CO Analyzer Zero/Span Results

Gas Type	Cylinder Concentrations	High MFC Device Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Low MFC Setting (cc/min)	Actual Flow (cc/min @ 760 mm Hg/25C)	Predicted Calibrator Delivered Concentration	Predicted Analyzer Response	Actual Analyzer Response	Percent Difference
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.9	-1.25
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.0	
Primary SRM SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.8	-1.48
Zero Gas	0	16000	15913.0	70	69.19	**0.00**	**0.07**	0.1	
Primary SRM	9982	16000	15913.0	70	69.19	**43.21**	**43.44**	42.9	-1.25
					Average Zero Gas Response =			**0.1**	
					Average Primary SRM Response =			**42.9**	

	Zero Gas Results	Span Gas Results
Std. Error = s/sqrt(n) =	0.03	0.03
Rrs/100 =	0.42866667	0.42866667
	Std. Error is okay.	Std. Error is okay.
Relative Difference (RD)=	-0.14%	-0.77%
	RD is okay.	RD is okay.

EPA Region 2 CO Assay

Assay Date: 11-Feb-10 **Assay Site:** EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ **Assay Conducted By:** Avi Teitz/Mustafa Mustafa

Test Set 1

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0	0.07	0.051	n/a
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	42.260	-2.2%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.500	0.7%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.700	3.5%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.600	-1.4%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	41.800	-3.4%
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.000	0.0%

Test Set 2

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	43.380	0.4%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.700	-1.2%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.800	3.7%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.400	0.5%
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0	0.07	0.080	n/a
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.130	0.3%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	41.900	-3.2%

Test Set 3

Vendor	Cylinder serial #	Cylinder Status	Vendor Certified Concentration	Diluent Gas MFC Setting (cc/min)	Diluent Gas Flow (cc/min)	Pollutant Gas MFC Setting (cc/min)	Pollutant Gas Flow (cc/min)	Flow Calculated CO Concentrations	Expected Analyzer Reading	Analyzer Readings (ppm)	Analyzer Readings Difference
Joe Blow	F12345678	Challenge Std. #5	2500	4000	3952.1	70.0	69.2	43.01	43.24	43.200	0.4%
BOC	E98765432	Challenge Std. #4	10000	16000	15913.0	70.0	69.2	43.29	43.52	42.000	-3.0%
Praxair	D12345678	Challenge Std. #3	5000	8000	7939.1	70.0	69.2	43.20	43.43	42.800	-0.9%
Scott	C98765432	Challenge Std. #2	5000	8000	7939.1	70.0	69.2	43.20	43.43	44.600	3.2%
Scott-Marrin	B12345678	Challenge Std. #1	5000	8000	7939.1	70.0	69.2	43.20	43.43	43.700	1.2%
Scott	ALM1234567	SRM 2639a	9982	16000	15913.0	70.0	69.2	43.21	43.44	42.260	-2.2%
Zero	n/a	n/a	0	16000	15913.0	0.0	0.0	0.00	0.07	0.900	n/a

QA Requirements Summary

	QA Requirement	Result	Status
SRM Gas Standards	Primary SRM Cylinder Expiration Date	31-Mar-11	Primary SRM Gas Standard OK
	Primary SRM Cylinder Pressure >150 psi	1200	Primary SRM cylinder pressure is OK
	SRM Dilution Check Cylinder Expiration Date	31-Mar-11	Dilution Check SRM Gas Standard OK
	Dilution Check SRM Cylinder Pressure >150 psi	900	Dilution check SRM cylinder pressure is OK
Laboratory Flow Standard	High Flow Standard Expiration Date	5-May-10	Standard OK
	Low Flow Standard Expiration Date	5-May-10	Standard OK
	Flow Standard Base Unit Expiration Date	5-May-10	Standard OK
Calibrator (mass flow controllers)	Calibrator Flow Calibration within 2 weeks of assay	9-Feb-10	Calibrator flow calibration within 2 weeks of assay
	Calibrated High Flow MFC Slope Range = 0.99 - 1.01	0.9999985	High MFC OK
	Calibrated Low Flow MFC Slope Range = 0.99 - 1.01	0.9999906	Low MFC OK
Carbon Monoxide Gas Analyzer	Analyzer Calibration within 2 week of assay	9-Feb-10	Analyzer calibration within 2 weeks of assay
	Estimate of Uncetainty < 1% at point #1 (>80% URL)	0.60%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #2	0.62%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #3	0.67%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #4	0.79%	Assay may be conducted at this concentration
	Estimate of Uncetainty < 1% at point #5 (~50% URL)	1.00%	Assay is invalid at this concentration
	Analyzer slope is within 0.98-1.02	1.0038	Analyzer Slope is acceptable
Dilution Check	Dilution Check Date within 2 weeks of assay	11-Feb-10	Dilution check within 2 weeks of assay
	Dilution Check Relative % Difference < 1%	-0.217%	Dilution Check RSD is OK
Day of Assay Zero/Span Check	Day of Assay Zero Check - Std. Error < 1%	Std. Error is okay.	Zero Gas Std. Error is OK
	Day of Assay Zero Check - Relative Difference < 5%	RD is okay.	Zero Gas RD is OK
	Day of Assay Span Check - Std. Error < 1%	Std. Error is okay.	Span Gas Std. Error is OK
	Day of Assay Span Check - Relative Difference <5%	RD is okay.	Span Gas RD is OK
Challenge Standard #1 Assay	Challenge Standard #1 Std. Error < 1%	The standard error is okay.	Challenge Standard #1 Std. Error is OK
	Challenge Standard #1 vendor certificate bias	2.17%	Challenge Std. #1 vendor certificate bias between 2-4%
Challenge Standard #2 Assay	Challenge Standard #2 Std. Error < 1%	The standard error is okay.	Challenge Standard #2 Std. Error is OK
	Challenge Standard #2 vendor certificate bias	4.93%	Challenge Std. #2 vendor certificate bias is 4% or greater
Challenge Standard #3 Assay	Challenge Standard #3 Std. Error < 1%	The standard error is okay.	Challenge Standard #3 Std. Error is OK
	Challenge Standard #3 vendor certificate bias	0.20%	Challenge Std. #3 vendor certificate bias < 2%
Challenge Standard #4 Assay	Challenge Standard #4 Std. Error < 1%	The standard error is okay.	Challenge Standard #4 Std. Error is OK
	Challenge Standard #4 vendor certificate bias	-1.91%	Challenge Std. #4 vendor certificate bias < 2%
Challenge Standard #5 Assay	Challenge Standard #5 Std. Error < 1%	The standard error is okay.	Challenge Standard #5 Std. Error is OK
	Challenge Standard #5 vendor certificate bias	1.60%	Challenge Std. #5 vendor certificate bias < 2%

Challenge Cylinder #3 Certificate

EPA Protocol Gas Verification Program

Date of Assay: **24-Mar-10**

Cylinder under Test:	**Scott-Marrin** **LL101544**
Pollutant Gas:	**Sulfur Dioxide**
Balance Gas:	**Nitrogen**
Cylinder Pressure After Assay:	**1780 psig**

Assayed SO2 Concentration =	**70.83**
Vendor Certified SO2 Concentration =	**71.20**
% bias =	**-0.52%**
95% uncertainty of analysis =	**0.29%**

Reference Gas:	**SRM 1694a** **CAL016709**
Expiration Date:	**11-Dec-15**
Analyst:	**Avi Teitz/Mustafa Mustafa**
Analytical Facility:	**EPA Region 2 Ambient Air Standards Laboratory, Edison, NJ**