EPA-600/R-97/121

EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF GASEOUS CALIBRATION STANDARDS

September 1997

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

EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF GASEOUS CALIBRATION STANDARDS

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

Section **Page**

List of Figures ix
List of Tables x
Acknowledgments xi
Glossary xiii

1 INTRODUCTION 1-1

2 EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF COMPRESSED GAS CALIBRATION STANDARDS 2-1

2.1 GENERAL INFORMATION 2-1
2.1.1 Purpose and Scope of the Protocol 2-1
2.1.2 Reference Standards 2-1
2.1.2.1 Gas Manufacturer's Intermediate Standard 2-4
2.1.2.2 Recertification of Reference Standards 2-5
2.1.3 Using the Protocol 2-5
2.1.4 Certification Documentation 2-5
2.1.5 Certification Label 2-6
2.1.6 Assay/Certification of Compressed Gas Calibration Standards 2-6
2.1.6.1 Incubation of Newly Prepared Compressed Gas Calibration Standards 2-6
2.1.6.2 Stability Test for Reactive Gas Mixtures 2-6

2.1.6.3 Certification Periods for Compressed Gas Calibration Standards 2-7
2.1.6.4 Minimum Cylinder Pressure 2-9
2.1.6.5 Assay/Certification of Multicomponent Compressed Gas Calibration Standards 2-9
2.1.7 Analyzer Calibration 2-10
2.1.7.1 Basic Analyzer Calibration Requirements 2-10
2.1.7.2 Analyzer Multipoint Calibration 2-10
2.1.7.3 Zero and Span Gas Checks 2-13
2.1.7.4 Reference Standards for Multipoint Calibrations and Zero and Span Gas Checks 2-14
2.1.7.5 Uncertainty of the Calibration Curve 2-14
2.1.8 Uncertainty of the Estimated Concentration of the Candidate Standard 2-15
2.1.9 Zero Gas 2-17
2.1.10 Accuracy Assessment of Commercially Available Standards 2-17

2.2 PROCEDURE G1: ASSAY AND CERTIFICATION OF A COMPRESSED GAS CALIBRATIOI WITHOUT DILUTION 2-18
2.1.1 Applicability 2-18

TABLE OF CONTENTS (continued)

Section **Page**

2.2.2 Limitations 2-18
2.2.3 Assay Apparatus 2-18
2.2.4 Pollutant Gas Analyzer 2-20
2.2.5 Analyzer Calibration 2-20
2.2.5.1 Multipoint Calibration 2-20
2.2.5.2 Analyzer Range 2-20
2.2.5.3 Linearity 2-20
2.2.5.4 Zero and Span Gas Checks 2-21
2.2.6 Assay Gases 2-22
2.2.6.1 Candidate Standard 2-22
2.2.6.2 Reference Standard 2-22
2.2.6.3 Zero Gas 2-23
2.2.7 Assay Procedure 2-23
2.2.8 Stability Test for Newly Prepared Candidate Standards 2-24
2.2.9 Certification Documentation 2-25
2.2.10 Recertification Requirements 2-25

2.3 PROCEDURE G2: ASSAY AND CERTIFICATION OF A COMPRESSED GAS CALIBRATIOI USING DILUTION 2-25
2.3.1 Applicability 2-25
2.3.2 Limitations 2-25
2.3.3 Assay Apparatus 2-26
2.3.4 Pollutant Gas Analyzer 2-29
2.3.5 Analyzer Calibration 2-29
2.3.5.1 Multipoint Calibration 2-29
2.3.5.2 Analyzer Range 2-30

2.3.5.3 Linearity 2-30
2.3.5.4 Zero and Span Gas Checks 2-30
2.3.6 Selection of Gas Dilution Flow Rates or Gas Concentration Settings 2-32
2.3.7 Flowmeter Type and Flowmeter Calibration 2-32
2.3.8 Assay Gases 2-33
2.3.8.1 Candidate Standard 2-33
2.3.8.2 Reference Standard 2-34
2.3.8.3 Zero Gas 2-34
2.3.9 Assay Procedure 2-34
2.3.10 Stability Test for Newly Prepared Standards 2-36
2.3.11 Certification Documentation 2-37
2.3.12 Recertification Requirements 2-37

3 EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF PERMEATION DEVIC CALIBRATION STANDARDS 3-1

TABLE OF CONTENTS (continued)

Section **Page**

3.1 GENERAL INFORMATION 3-1
3.1.1 Purpose and Scope of the Protocol 3-1
3.1.2 Reference Standards 3-1
3.1.3 Selecting a Procedure 3-2
3.1.4 Using the Protocol 3-3
3.1.5 Certification Documentation 3-3
3.1.6 Certification Label 3-4
3.1.7 Assay/Certification of Candidate Permeation Device Calibration Standards 3-4
3.1.7.1 Permeation Device Design 3-4
3.1.7.2 Precautions for Use and Storage of Permeation Devices 3-4
3.1.7.3 Equilibration of Newly Prepared Permeation Devices 3-5
3.1.7.4 Certification Conditions for Permeation Device Calibration Standards 3-5
3.1.8 Technical Variances 3-5

3.2 PROCEDURE P1: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATIO STANDARDS REFERENCED TO A PERMEATION DEVICE REFERENCE STANDARD 3-6
3.2.1 Applicability 3-6
3.2.2 Limitations 3-6
3.2.3 Assay Apparatus 3-7
3.2.4 Pollutant Gas Analyzer 3-9
3.2.5 Analyzer Calibration 3-9
3.2.5.1 Multipoint Calibration 3-9
3.2.5.2 Analyzer Range 3-10
3.2.5.3 Linearity 3-10
3.2.5.4 Zero and Span Gas Checks 3-10

3.2.6 Selection of Gas Dilution Flow Rates 3-10
3.2.7 Flowmeter Type and Flowmeter Calibration 3-10
3.2.8 Permeation Devices 3-11
3.2.8.1 Candidate Standard 3-11
3.2.8.2 Reference Standard 3-11
3.2.8.3 Zero Gas 3-11
3.2.9 Assay Procedure 3-12
3.2.10 Stability Test for Newly Prepared Permeation Devices 3-14
3.2.11 Certification Documentation 3-14
3.2.12 Recertification Requirements 3-15

TABLE OF CONTENTS (continued)

Section **Page**

3.3 PROCEDURE P2: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATIO STANDARDS REFERENCED TO A COMPRESSED GAS REFERENCE STANDARD 3-15
3.3.1 Applicability 3-15
3.3.2 Limitations 3-15
3.3.3 Assay Apparatus 3-15
3.3.4 Pollutant Gas Analyzer 3-17
3.3.5 Analyzer Calibration 3-18
3.3.5.1 Multipoint Calibration 3-18
3.3.5.2 Analyzer Range 3-19
3.3.5.3 Linearity 3-19
3.3.5.4 Zero and Span Gas Checks 3-19
3.3.6 Selection of Gas Dilution Flow Rates 3-19
3.3.7 Flowmeter Type and Flowmeter Calibration 3-19
3.3.8 Candidate Standard 3-20
3.3.9 Reference Standard 3-20
3.3.10 Zero Gas 3-21
3.3.11 Assay Procedure 3-21
3.3.12 Equilibrium Test for Newly Prepared Permeation Devices 3-24
3.3.13 Certification Documentation 3-24
3.3.14 Recertification Requirements 3-24

3.4 PROCEDURE P3: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATIO STANDARDS REFERENCED TO A MASS REFERENCE STANDARD 3-24
3.4.1 Applicability 3-24
3.4.2 Limitations 3-24
3.4.3 Assay Apparatus 3-25
3.4.3.1 Analytical Balance 3-25
3.4.3.2 Temperature-Controlled Chamber 3-25
3.4.3.3 Electrostatic Charge Neutralization 3-27
3.4.4 Weighing Interval 3-27
3.4.5 Assay Procedure 3-28
3.4.6 Number of Weighings of the Candidate Standard 3-29

3.4.7 Calculation of Certified Permeation Rate 3-29
3.4.8 Uncertainty of Certified Permeation Rate for Candidate Standard 3-31
3.4.9 Certification Documentation 3-31
3.4.10 Recertification Requirements 3-31

4 REFERENCES 4-1

TABLE OF CONTENTS (continued)

Appendix		Page
A	INSTRUCTIONS FOR CALIBRATION WORKBOOK	A-1
B	INSTRUCTION FOR PERMEATION RATE WORKBOOK	B-1
C	CALCULATION OF TOTAL ANALYTICAL UNCERTAINTY	C-1
D	MATRIX NOTATION	D-1

LIST OF FIGURES

Number		Page
2-1	Example regression curve and confidence bands from multipoint calibration	2-12
2-2	One possible design of the apparatus for the assay of compressed gas calibration standards without dilution (Procedure G1)	2-19
2-3	One possible design of the apparatus using flow controllers for assay of compressed gas calibration standards with dilution (Procedure G2)	2-27
2-4	One possible design of the apparatus using a gas dilution system for assay of compressed gas calibration standards with dilution (Procedure G2)	2-28
3-1	One possible design of the apparatus for the assay of permeation device calibration standards referenced to a permeation device reference standard (Procedure P1)	3-8
3-2	One possible design of the apparatus for the assay of permeation device calibration standards referenced to a compressed gas reference standard (Procedure P2)	3-16
3-3	Chamber for maintaining permeation tubes at constant temperature	3-26
3-4	Example of spreadsheet graphic output for calculating permeation rates	3-30

LIST OF TABLES

Number		Page
2-1	SUMMARY OF COMPRESSED GAS SRMs THAT ARE AVAILABLE FROM NIST	2-2
2-2	SUMMARY OF COMPRESSED GAS PRMs THAT ARE AVAILABLE FROM NMi	2-3
2-3	CERTIFICATION PERIODS FOR COMPRESSED GAS CALIBRATION STANDARDS IN ALUMIN CYLINDERS THAT ARE CERTIFIED UNDER THIS PROTOCOL	2-8
2-4	SOME LINEARIZING TRANSFORMATIONS FOR MULTIPOINT CALIBRATION DATA	2-16
3-1	NIST SRM PERMEATION DEVICE REFERENCE STANDARDS	3-2

ACKNOWLEDGMENTS

The information in this document has been funded wholly by the U.S. Environmental Protection Agency (EPA) under Contract No. 68D40091 to the Research Triangle Institute (RTI), Research Triangle Park, North Carolina.

This traceability protocol was prepared by Robert S. Wright and Michael J. Messner of RTI under RTI Project No. 91U-6699-208. It is a revision of an earlier protocol that was prepared in 1993 by the same authors. The authors thank the EPA work assignment manager, Berne I. Bennett, for his guidance and technical discussion as the protocol was being written. The authors also thank the following RTI staff members who provided administrative, technical, editorial, word processing, and graphic arts support: Malcolm J. Bertoni, Michael Y. Cross, W. Cary Eaton, Tonda J. Gentry, Beryl C. Pittman, Helen M. Reading, Sue S. Preston, and Jan L. Shirley.

This protocol was reviewed by personnel of EPA, the National Institute of Standards and Technology (NIST), and the Netherlands Measurement Institute (NMi) as it was being prepared. The authors wish to thank the following individuals for their technical assistance:

Pamela M. Chu (NIST)
Ed W.B. DeLeer (NMi)
Willliam D. Dorko (NIST)
David L. Duewer (NIST)
Gerald D. Mitchell (NIST)
John T. Schakenbach (EPA)
Rob Wessel (NMi)

Numerous comments from specialty gas producers provided useful comments and suggestions for revisions to this protocol. The authors thank the following organizations for their assistance:

Airgas, Inc.
Air Liquide America Corporation
Air Products and Chemicals, Inc.
BOC Gases
Matheson Gas Products
MG Industries
Praxair, Inc.
Scott-Marrin, Inc.
Scott Specialty Gases, Inc.
Spectra Gases, Inc.

GLOSSARY

ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
GMIS	Gas Manufacturer's Intermediate Standard
ILAC	International Laboratory Accreditation Program
ISO	International Standardization Organization
NIST	National Institute of Standards and Technology
Nmi	Netherlands Measurement Institute
NTRM	NIST Traceable Reference Material
NVLAP	National Voluntary Laboratory Accreditation Program
PRM	Primary Reference Material
RGM	Research Gas Mixture
SRM	Standard Reference Material

SECTION 1

INTRODUCTION

In 1993, the U.S. Environmental Protection Agency (EPA) in Research Triangle Park, North Carolina, revised its 1987 version of its traceability protocol for the assay and certification of compressed gas and permeation-device calibration standards.[1,2] 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.[3-6]

As the protocol was being revised, the 1987 version was published in the January 11, 1993, issue of the *Federal Register*. It was inserted as Appendix H to 40 CFR Part 75, which concerns the Acid Rain Program. In April 1996, EPA's Acid Rain Program suggested that the 1987 and 1993 versions of the protocol be consolidated into a single protocol. In discussions at that time, RTI suggested that the protocol be revised in a manner that would allow EPA Protocol Gases to be produced either with the higher accuracy (within ±2 percent) needed by EPA's Acid Rain Division or with less stringent accuracy requirements that might be acceptable to other users. In 1997, RTI solicited additional suggested revisions from specialty gas producers and other interested parties.

The purpose of this work assignment was to revise the statistical procedures in the 1993 version of the protocol and to consolidate its two published versions in order to make the revised protocol useful to EPA's Acid Rain Division as well as other users. Improvement of the statistical procedures had the highest priority.

The current revision has several significant changes from the 1993 version as listed below:

1. Statistical techniques are used to calculate the total uncertainty of the candidate standard. Data from the multipoint calibration and the assays are used in these calculations (see Section 2.1.4);

2. The uncertainty of reference standards is now included in the calculation of the total uncertainty of the candidate standard (see Section 2.1.2);

3. Statistical techniques are used to calculate the stability of candidate standards. The intermediate performance standard of 1 percent agreement between assays has been deleted (see Section 2.1.6.2);

4. Statistical spreadsheets were developed to assist in these calculations, but equivalent statistical techniques may also be used. These spreadsheets replace most of the manual calculations required in the 1993 version of the protocol (see Appendices A through D).

5. Multipoint calibration data may be fitted to straight-line, quadratic, cubic, or quartic linear regression models by the spreadsheets, although the use of cubic and quartic models is discouraged (see Appendix A);

6. If a quadratic or higher-order model is used to fit the multipoint calibration data, at least two reference standards, having different concentrations, must be measured during the assays (see Section 2.2.7);

7. The correction for minor calibration drift following the multipoint calibration is embedded in the spreadsheets' calculation of the uncertainty of a single assay;

8. Primary Reference Standards from the Netherlands Measurement Institute (NMi) are accepted as being equivalent to SRMs from NIST (see Section 2.1.2);

9. The analyst may substitute a low-concentration reference standard in the place of the zero gas during assays of the candidate standard (see Section 2.1.9);

10. A summary of EPA's audit results from 1992 to the present is available at an EPA website, http://www.epa.gov/ttn (see Section 2.1.10);

11. A strip chart recorder is no longer required as part of the assay apparatus, but a high-precision data acquisition system must produce an electronic or paper record of the analyzer's response during assays. This record must be maintained for 3 years after the standard's certification date (see Section 2.2.4).