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Standard Guide for Intercomparing Permeation Tubes to Establish Traceability[1]

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ε[1] NOTE—Editorial corrections were made throughout in December 2014.

1. Scope

1.1 This guide covers two procedures for establishing the permeation rate of a permeation tube and defining the uncertainty of the rate by comparison to National Institute of Standards and Technology's Standard Reference Materials (SRM).

1.2 Procedure A consists of a direct comparison of the permeation rate of the device undergoing calibration with that of an SRM.

1.3 Procedure B consists of a gravimetric calibration process in which a certified permeation tube is used as a quality control for the measurements.

1.4 Both procedures are limited to the case where a suitable certified permeation device is available.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (See 8.2 on Safety Precautions.)

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3249 Practice for General Ambient Air Analyzer Procedures

D3609 Practice for Calibration Techniques Using Permeation Tubes

D3631 Test Methods for Measuring Surface Atmospheric Pressure

E1 Specification for ASTM Liquid-in-Glass Thermometers

E319 Practice for the Evaluation of Single-Pan Mechanical Balances

E617 Specification for Laboratory Weights and Precision Mass Standards

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this guide, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *working standard*—a standard used in the laboratory or field for periodic standardization of a measuring instrument.

4. Summary of Guide

4.1 *Procedure A*—A certified SRM permeation source, obtained from the National Institute of Standards and Technology is used to calibrate a continuous analyzer. The analyzer is then used to measure the concentration of a gaseous mixture generated from the permeation tube under calibration. Equations are provided that permit calibration of the permeation rate of the latter from the test data.

4.2 *Procedure B*—The permeation source is calibrated, gravimetrically, using temperature and mass standards traceable to NIST standards. The validity of the calibration is confirmed by concurrently measuring the permeation rate of a Certified Reference Material (CRM).

5. Significance and Use

5.1 The accuracy of air pollution measurements is directly dependent upon accurate calibrations.

5.2 Such measurements gain accuracy and can be intercompared when the measurement procedures are traceable to national measurement standards.

5.3 This guide describes procedures for enhancing the accuracy of air pollution measurements which may be specified by those organizations requiring traceability to national standards.

[1] This guide is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.01 on Quality Control.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

6. Apparatus

6.1 For apparatus used in the calibration of permeation devices, refer to Practice D3609.

6.1.1 The thermometers used shall conform to Specification E1 and shall have calibration certificates traceable to the NIST. Measurement uncertainty should be 0.1°C or less.

6.1.2 The mercury barometer shall conform to Test Methods D3631.

6.2 *Apparatus for Procedure A:*

6.2.1 *Analytical Instruments*—An analytical instrument responsive to the permeant with the following minimum performance specifications:

Noise	1 % of full-scale
Zero drift	±4 % of full-scale per day
Span drift	±3 % of full-scale per day
Range	0 to 0.5 ppm (or appropriate for source strength)

6.2.2 Continuous strip chart recorder with the following minimum performance specifications:

Uncertainty component	0.33 × (0.25 % full-scale deflection)
Chart width	no less than 6 in.
Time for full-scale travel	1 s

NOTE 1—ISO GUM[3] points out that with approximately normal plotted points, the above maximum 3 × standard deviations is equivalent to >99 % of plotted points lying within ± (0.25 % full-scale deflection) of true values.

6.3 *Apparatus for Procedure B:*

6.3.1 Analytical balance, meeting the requirements of Practices E319 and D3609.

6.3.2 Analytical weights meeting the requirements of Specification E617 and having a calibration certificate traceable to the NIST.

7. Materials

7.1 Refer to Practice D3609.

7.2 CRM Permeation Device.[4]

8. Precautions

8.1 *Procedural Precautions:*

8.1.1 The procedural precautions described in Practice D3609 are applicable to the present guide.

8.1.2 When possible, the permeation device should be compared to the CRM using the same system with identical flow and temperature conditions. Unpredictable errors may be introduced if permeation devices are compared at widely different temperatures and flow rates (pertains to Procedure A). Intercomparisons are valid only at temperatures for which the CRM tube is calibrated.

8.1.3 Equilibration of the permeation device, the calibration equipment, and the analytical system must be assured, prior to use. During storage, avoid exposing tubes to high humidities or wide variations in temperature, that may permanently alter the permeation rate.

8.2 *Safety Precautions:*

8.2.1 For precautions concerning the use of analytical instruments and of cylinders containing pressurized gases, see Practice D3249.

9. Calibration and Standardization

9.1 *Procedure A:*

9.1.1 Set up a gas generation system using a Certified Reference Material (CRM) permeation tube and apparatus and procedure such as described in Practice D3609. Equilibrate at the desired temperature of calibration.

9.1.2 Optimize the performance of the analytical instrument according to the manufacturer's instructions.

9.1.3 Using dry air or nitrogen, set the zero point of the instrument.

9.1.4 Use the gas generation system to provide gas concentrations corresponding to 20, 40, 60, and 80 % of full-scale readings. Record the concentration and respective readings. Repeat the measurements in random order.

9.1.5 Plot concentration versus instrument readings and draw the line of best fit, or alternatively fit by linear least squares regression. Calculate the slope (ppm(v)/scale reading) and standard deviation estimate s_{cal}, expressed as µg/min.

9.1.5.1 If any point deviates by more than ±1 % from the line of best fit, repeat the calibration.

9.2 *Procedure B:*

9.2.1 The standard masses and the thermometer used must have a valid calibration certificate or be calibrated prior to use.

10. Procedure

10.1 *Procedure A:*

10.1.1 Place test permeation device in the system, equilibrate at the temperature of calibration, and generate gas mixtures corresponding approximately to 20, 40, 60, and 80 % of full scale readings, respectively.

10.1.2 Record the instrument readings for each gas mixture.

10.1.3 Using calibration curves described in 9.1.5, calculate the concentrations of the gas mixtures.

10.1.4 Calculate the permeation rates as described in 11.1.

10.1.5 Repeat the measurements of 10.1.1 in random order and record as in 10.1.2.

10.2 *Procedure B:*

10.2.1 Maintain the permeation device at constant temperature, T, during the sequence of measurements described as follows:

10.2.2 Weigh permeation device, periodically recording the mass and time of weighing, as described in Practice D3609.

10.2.3 Calculate the mass loss per unit of time in the units of µg/min at temperature, T.

10.2.4 Calibrate a CRM permeation tube using the same procedure and concurrently with the test permeation device.

11. Calculations

11.1 *Procedure A:*

11.1.1 Calculate the permeation rate for each of the eight measurements, using the following equation:

$$R = C_{ppm(v)} \frac{F \times MW}{MV} \quad (1)$$

[3] ISO GUM, *Guide to the Expression of Uncertainty in Measurement*, International Organization for Standardization (ISO), available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[4] Certified permeation tubes may be obtained from NIST currently only by special order from the Office of Standard Reference Materials, National Institute of Standards and Technology, Washington, DC 20234.

where:

R = permeation rate, µg/min,
$C_{ppm(v)}$ = measured concentration, ppm(v) (by volume),
F = total flow rate of gas (L/min),
MW = molecular weight of permeant, and
MV = molecular volume (24.47 L at 25°C and 101.3 kPa).

11.1.2 Calculate the mean $\bar{R}$ of measured rates and the standard deviation, s_R. The temperature corresponding to $\bar{R}$ must be stated.

11.1.3 Calculate the standard deviation s of $\bar{R}$ itself:

$$s = \sqrt{s_{cal}^2/n + s_R^2/n} \quad (2)$$

where n is the number (8) of R measurements or calibration data points.

11.1.4 The uncertainty U in the measurement $\bar{R}$ may be expressed in several ways, depending on the needs of the user. The purpose of the (expanded) uncertainty U is to bracket the certified-mean R_{true} by $\bar{R} \pm U$ at specified confidence. The degree of confidence in the minimization of bias of the specific SRM used for calibration relative to the certified-mean R_{true} depends on the application. Related material presented in (11.1.4) may be found in NMAM.[5]

11.1.4.1 If U, at high (95 %) confidence in the specific CRM used for calibration, is to provide intervals bracketing R_{true} at greater than given confidence (also 95 %) in the measurement $\bar{R}$, then U may be taken to equal:

$$U = 1.960 \cdot u_{CRM} + t_{\upsilon,\ 0.95} \cdot s \quad (3)$$

where u_{CRM} is the ratio of the uncertainty of the CRM calibration to the coverage factor, both values stated on the CRM certificate. υ is the number of degrees of freedom in s^2 and $t_{\upsilon,0.95}$ is the student-t 95 %-quantile (giving single-sided 95 % confidence limits). Here, $\upsilon = 2 \times (n - 1) = 14$ if the analyzer output is closely proportional to its input, resulting in $t_{14,0.95} = 1.761$. Eq 3 holds when the CRM-|bias| confidence limit $1.960 \cdot u_{CRM}$ is comparable or larger than $s / t_{\upsilon,0.95}$. For small u_{CRM}, the uncertainty U may be calculated as:

$$U = t_{\upsilon,0.975} \cdot \sqrt{1.960^2\, u_{CRM}^2 \cdot (1 - \upsilon^{-1})/(1 + t_{\upsilon,\ 0.975}^2 \cdot \upsilon^{-1}) + s^2} \quad (4)$$

$$\approx t_{\upsilon,\ 0.975} \cdot \sqrt{1.960^2\, u_{CRM}^2 + s^2},\ if\ \upsilon >> 1$$

$$(t_{14,\ 0.975} = 2.145).$$

11.1.4.2 If only *mean* confidence in the CRM is required, then U may be approximated simply as:

$$U = 2 \cdot \sqrt{u_{CRM}^2 + s^2} \quad (5)$$

NOTE 2—The above expressions assume that the calibrations of Section 9 and measurements of 10.1 are made within a time interval such that instrumental drift is not significant. This requires that the permeation devices to be calibrated should be equilibrated at the temperature of measurement before insertion into the system. If this is not the case, uncertainty due to drift must be estimated and included because of the large dependence of the permeation rates on the temperature. The T-uncertainty component $u_{\bar{R},T}$ (the standard deviation) due to drift would then be estimated, using the mean temperature coefficient $\Delta R / \Delta T$ of standard and reference tube. The standard tube's temperature coefficient may be listed in the CRM certificate, whereas the candidate tube's coefficient would be either measured or a conservative value of 10 % of the permeation rate in accordance with Practice D3609 (°C), adopted. Then, $u_{\bar{R},T}$ is estimated by:

$$u_{\bar{R},T} = |\Delta R/\Delta T| \cdot \sigma_T \quad (6)$$

where σ_T (°C) is an estimate of the temperature-drift standard deviation. If $u_{\bar{R},T}$ is of the order of $s_{cal}/\sqrt{n}$ or $s_R/\sqrt{n}$, then $u_{\bar{R},T}$ would be pooled into s, adjusting the student-t quantile with an effective number of degrees of freedom, accordingly (as described in ISO GUM).

NOTE 3—The uncertainty as expressed in Eq 5 is in the form considered in ISO GUM with coverage factor equal to 2, whereas strongly controlling the bias inherent in any specific calibration standard results in the slightly different form of Eq 4.

11.2 *Procedure B:*

11.2.1 Plot successive masses versus the corresponding times. Fit a straight line to the points by the method of least squares. The slope is the desired rate, $\bar{R}$. Calculate the standard deviation, s, of the slope.

11.2.2 Express uncertainty by the following equation:

$$U = 2 \cdot \sqrt{s^2 + (0.1/°C \cdot \sigma_t)^2} \quad (7)$$

11.2.3 The mean permeation rate, $\bar{R}_{CRM}$ measured for the CRM permeation tube must agree with the certified value in accordance with the user's performance standards, accounting for the limits of uncertainty of the measurement, as calculated by 11.2.2, in order to validate the calibration.

12. Keywords

12.1 intercomparison; permeation tube; standard reference material; traceability

[5] *NIOSH Manual of Analytical Methods (NMAM)*, Chapter P, Measurement Uncertainty and NIOSH Method Accuracy Range, available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, or online at www.cdc.gov/niosh.