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

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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 *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:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 3249 Practice for General Ambient Air Analyzer Procedures[2]

D 3609 Practice for Calibration Techniques Using Permeation Tubes[2]

D 3631 Test Methods for Measuring Surface Atmospheric Pressure[2]

E 1 Specification for ASTM Thermometers[3]

E 319 Practice for the Evaluation of Single-Pan Mechanical Balances[4]

E 617 Specification for Laboratory Weights and Precision Mass Standards[4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this guide, refer to Terminology D 1356.

3.1.2 *Definitions of Terms Specific to This Standard*:

3.1.2.1 *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 NIST SRM.

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.

6. Apparatus

6.1 For apparatus used in the calibration of permeation devices, refer to Practice D 3609.

6.1.1 The thermometers used shall conform to Specification E 1 and shall have calibration certificates traceable to the NIST. Measurement uncertainty should be 0.1°C or less.

[1] This guide is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.01 on Quality Control.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 14.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

6.1.2 The mercury barometer shall conform to Test Methods D 3631.

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
Range	0 to 0.5 ppm (or appropriate for source strength)

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

Accuracy	±0.25 % full-scale deflection
Chart width	no less than 6 in.
Time for full-scale travel	1 s

6.3 *Apparatus for Procedure B*:

6.3.1 Analytical balance, meeting the requirements of Practices E 319 and D 3609.

6.3.2 Analytical weights meeting the requirements of Specification E 617 and having a calibration certificate traceable to the NIST.

7. Materials

7.1 Refer to Practice D 3609.

7.2 NIST SRM 1625, 1626, or 1627 Sulfur Dioxide Permeation Device, or NIST SRM 1629, Nitrogen Dioxide Permeation Device.[5]

8. Precautions

8.1 *Procedural Precautions*:

8.1.1 The procedural precautions described in Practice D 3609 are applicable to the present guide.

8.1.2 When possible, the permeation device should be compared to the SRM 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 SRM 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 D 3249.

9. Calibration and Standardization

9.1 *Procedure A*:

9.1.1 Set up a gas generation system using a permeation tube and apparatus and procedure such as described in Practice D 3609. 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 and express as ppm/scale reading.

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 Weight of permeation device, periodically recording the weight and time of weighing, as described in Practice D 3609.

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

10.2.4 Calibrate an NIST Certified SRM 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:

$$R = C_{\text{ppm}} \frac{F \times MW}{MV} \tag{1}$$

where:

R = permeation rate, µg/min,
C_{ppm} = measured concentration, ppm,
F = total flow rate of gas (L/min),
MW = molecular weight of permeant, and
MV = molecular volume of permeant.

11.1.2 Calculate mean of measured rates, $\bar{R}$, and standard deviation, s.

11.1.3 Express the uncertainty of the calibration as follows:

[5] Certified permeation tubes may be obtained from the Office of Standard Reference Materials, National Institute of Standards and Technology, Washington, DC 20234.

$$\text{Uncertainty} = \pm \left[U_{srm} + U_T \frac{\Delta R}{\Delta T} + \frac{ts}{\sqrt{n}} \right] \quad (2)$$

where:

U_{srm} = uncertainty of SRM calibration as stated on certificate,

$\frac{\Delta R}{\Delta T}$ = temperature coefficient of the permeation rate (supplied by NIST for SRM permeation tube),

U_T = estimated uncertainty in temperature of permeation device, expressed in °C,

n = number of measured values of R,

t = student constant for n-1 degrees of freedom, and

s = standard deviation.

In the above, the temperature corresponding to $\bar{R}$ must be stated.

NOTE 1—This expression assumes 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 instrumental drift must be estimated and included.

11.2 *Procedure B*:

11.2.1 Calculate R for each successive weighing according to the following equation:

$$R = \frac{\Delta \text{w}}{\Delta \text{min}} \quad (3)$$

where:

Δw = loss in weight, expressed in µg over time interval, Δmin, expressed in minutes.

11.2.2 Calculate the mean of the measured rates, $\bar{R}$, and the standard deviation, s.

11.2.3 Alternatively, plot successive weighings versus the corresponding times. Fit a straight line to the points by the method of least squares. The slope is the desired note, $\bar{R}$. Calculate the standard deviation, s, of the slope.

11.2.4 Express uncertainty of calibration by the following equation:

$$\text{Uncertainty} = \frac{ts}{\sqrt{n}} + \bar{R} \times 0.1 \times U_T \quad (4)$$

where U_T, t, s, and n are the same as in 11.1.3.

11.2.5 The mean permeation rate, $\bar{R}$, measured for the NIST permeation tube must agree with the certified value within the limits of uncertainty of the measurement, as calculated by 11.2.3, in order to validate the calibration.

12. Keywords

12.1 intercomparison; permeation tube; standard reference material; traceability