

## SECTION 3

### EPA TRACEABILITY PROTOCOL FOR ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATION STANDARDS

#### 3.1 GENERAL INFORMATION

##### 3.1.1 Purpose and Scope of the Protocol

This protocol describes three procedures for assaying the permeation rate of a permeation device calibration standard and for certifying that the assayed permeation rate is traceable to National Institute of Standards and Technology (NIST) reference standards. This protocol is mandatory for certifying the permeation device calibration standards used for the pollutant monitoring that is required by the regulations of the *Code of Federal Regulations*, Chapter 40, Parts 50 and 58<sup>3,4</sup> for the calibration and audit of ambient air quality analyzers. This protocol covers the assay and certification of sulfur dioxide (SO<sub>2</sub>) and nitrogen dioxide (NO<sub>2</sub>) permeation device calibration standards. This protocol may be used by permeation device producers, standard users, or other analytical laboratories. The assay procedure may involve the comparison of these standards to permeation device reference standards (i.e., Procedure P1), to compressed gas reference standards (i.e., Procedure P2), or to mass reference standards (i.e., Procedure P3).

##### 3.1.2 Reference Standards

The permeation device reference standards that may be used under this protocol are NIST Standard Reference Material (SRM) numbers 1625 and 1626. These SRMs (listed in Table 3.1) are permeation tubes containing SO<sub>2</sub>. In the future, NIST may develop additional SRMs, which may be used as reference standards under this protocol.

The compressed gas reference standards that may be used under this protocol are NIST SRMs, Netherlands Measurement Institute Primary Reference Materials (NMI PRMs) that are equivalent to SRMs, NIST traceable reference materials (NTRMs), or gas manufacturer's intermediate standards (GMISs). These standards are described in Subsection 2.1.2 of this report.

The uncertainty of SRMs, NTRMs, and PRMs is expressed as a 95-percent confidence interval, which is the one-sigma uncertainty multiplied by a coverage factor almost always equal to 2.<sup>9</sup> This estimate includes allowances for the uncertainties of known sources of systematic error as well as the random error of measurement. A value of one-half of the stated uncertainty of these reference standards should be used in calculating the total analytical uncertainty of standards that are certified under this protocol (see Appendix C).

Mass reference standards that may be used under this protocol must be traceable to NIST mass standards.<sup>18-20</sup> Additionally, they must have an individual tolerance of no more than 0.05 mg. Examples of mass reference standards that meet these specifications are American National Standards Institute/American Society for Testing and Materials (ANSI/ASTM) Classes 1, 3, and 4. The mass reference

**TABLE 3-1. NIST SRM PERMEATION DEVICE REFERENCE STANDARDS**

NIST SRM no.	Permeation device type	Device length (cm)	Nominal permeation rate at 30 °C (µg/min)	Nominal concentration (in µmol/mol) at various dilution gas flow rates (L/min)		
				1	5	10
1625	Sulfur dioxide	10	3.7	1.4	0.28	0.14
1626	Sulfur dioxide	5	2.1	0.8	0.16	0.08

standards must be recalibrated on a regular basis (e.g., yearly) at a NIST-accredited State weights and measures laboratory or at a calibration laboratory that is accredited by the National Voluntary Laboratory Accreditation Program (NVLAP),<sup>10,11</sup> which is administered by NIST, or by the International Laboratory Accreditation Conference (ILAC). The recalibration frequency is to be determined from records of previous recalibrations of these standards.

Two separate sets of mass reference standards are recommended. Working calibration standards should be used for routine permeation device weighings and should be kept next to the analytical balance in a protective container. Laboratory primary standards should be handled very carefully and should be kept in a locked compartment. The working standards should be compared to the laboratory primary standards every 3 or 6 months to check for mass shifts associated with handling or contamination. The current masses of the working standards as traced to the laboratory primary standards should be recorded in a laboratory notebook and should be used to check the calibration of the analytical balance.

Always use smooth, nonmetallic forceps for handling mass reference standards. The standards are handled only with these forceps, which are not used for any other purpose. Mark these forceps to distinguish them from the forceps that are used to handle permeation devices. Handle the standards carefully to avoid damage that may alter their masses.

The temperature reference standards that may be used under this protocol must be liquid-in-glass thermometers having scale tolerances and uncertainties that conform to NIST Special Publication 250-23.<sup>21</sup> They must have an uncertainty of no more than 0.05 (°C). The thermometers must have serial numbers etched or permanently marked into the glass and a manufacturer's calibration certificate of traceability to NIST standards. They must be recalibrated on a regular schedule (e.g., yearly) according to NIST guidelines<sup>22</sup> by the user, a NIST-accredited State weights and measures laboratory, or an NVLAP- or ILAC-accredited calibration laboratory.

### 3.1.3 Selecting a Procedure

Procedures P1 and P2 are applicable to the assay and certification of candidate permeation device calibration standards using an ambient air quality analyzer. Procedure P1 provides for the assay to be referenced to a permeation device reference standard. Procedure P2 provides for the assay to be referenced to a compressed gas reference standard.

Procedure P3 is applicable to the assay and certification of candidate standards using an analytical balance. This procedure provides for the assay to be referenced to a mass reference standard.

### 3.1.4 Using the Protocol

The assay/certification protocol described here is designed to minimize both systematic and random errors in the assay process. Therefore, the protocol should be carried out exactly as it is described. The assay procedures in this protocol include one possible design for the assay apparatus. The analyst is not required to use this design and may use alternative components and configurations that produce equivalent-quality measurements. Nonreactive materials (e.g., Teflon<sup>®</sup>, stainless steel, or glass) and clean, noncontaminating components should be used in those portions of the apparatus that are in contact with the gas mixtures being assayed.

### 3.1.5 Certification Documentation

Each certified permeation device calibration standard must be documented in a written certification report and this report must contain at least the following information:

1. Permeation device identification number;
2. The contents of the permeation device;
3. Certified permeation rate (in nanograms (ng) per minute);
4. The certification temperature (in °C to the nearest 0.1°);
5. The dilution gas (i.e., air or nitrogen) used during the assay (for procedures P1 and P2);
6. Date of the assay/certification;
7. Identification of the reference standards used in the assay: NIST SRM number, NIST sample number, and certified concentration or permeation rate for an SRM; cylinder identification number and certified concentration for an SRM-equivalent PRM, an NTRM or GMIS; manufacturer, model number and serial number for a mass or temperature reference standard. The certification documentation must identify the type of reference standard used in the assay;
8. Statement that the assay/certification was performed according to this protocol and that lists the assay procedure (e.g., Procedure P1) used;
9. The analytical method that was used in the assay;
10. Identification of the laboratory where the standard was assayed and certified;
11. Chronological record of all certifications for the standard by the certifying laboratory;
12. A statement that the standard will retain its certification only as long as 5 percent of the original liquid weight or a visible amount of liquid remains in it;
13. The environmental exposure conditions (e.g., temperature and moisture) that will invalidate the certification; and
14. A statement of the overall analytical uncertainty estimate associated with the assay of the candidate standard. The estimate must include the uncertainty associated with the reference standard.

This certification documentation must be given to the purchaser of the standard. The permeation device producer must maintain laboratory records and certification documentation for 3 years after the standard's certification date. A permeation device producer or other vendor may redocument an assayed and certified standard that it has purchased from another permeation device producer and that it wishes to sell to a third party. However, the new certification documentation must clearly list the permeation device producer or other laboratory where the standard was assayed.

### **3.1.6 Certification Label**

The permeation device calibration standard must be labeled with its identification number.

### **3.1.7 Assay/Certification of Candidate Permeation Device Calibration Standards**

#### **3.1.7.1 Permeation Device Design—**

Permeation devices are designed and constructed in various ways, but all devices consist of a sealed chamber containing liquified gas and a permeable area through which the gas is allowed to permeate. The permeated gas is swept and diluted with a measured volumetric flow rate of dry air or nitrogen to create a quantitative concentration of the pollutant gas.

#### **3.1.7.2 Precautions for Use and Storage of Permeation Devices—**

The permeation rate of all permeation devices is critically dependent on temperature; a permeation device is useful as a concentration standard only when its temperature is precisely controlled and accurately measured, and an accurately metered dilution gas flow rate is provided.

The inaccuracy of gaseous pollutant concentration standards that are produced by permeation devices may increase due to physical or chemical sorption of the permeated gas in the permeation system. This sorption will have a larger effect on the inaccuracy as the concentration decreases. Nonreactive materials (e.g., Teflon<sup>®</sup>, stainless steel, or glass) and clean, noncon-taminating components should be used in those portions of the permeation system that are in contact with the permeated gas.

The reproducibility of the certified permeation rate of a permeation device may be adversely affected by exposure of the device to temperatures greater than the specified operating or storage temperature range for the device or by exposure to excessive moisture. NO<sub>2</sub> permeation devices must be stored under dry conditions and preferably at a temperature between 20 and 35 °C, or as otherwise recommended by the manufacturer. SO<sub>2</sub> permeation devices may be refrigerated for storage.

It appears that there is a limited temperature range at which NO<sub>2</sub> permeation devices can be used as standards. This temperature range is conservatively given as 20 to 35 °C.<sup>23</sup> Low or high temperature storage of NO<sub>2</sub> permeation devices is not recommended.

NO<sub>2</sub> permeation devices should be stored in and used in dry dilution gas. One study showed that NO<sub>2</sub> permeation rates were significantly lower in moderately humid air (i.e., 30 to 40 percent relative humidity) than in dry air on the preceding day.<sup>24</sup> Furthermore, the permeation rates did not return to the original levels after dry air had passed over the device for 24 hours. Another study found that NO<sub>2</sub> concentrations from a permeation device declined by about one-third as relative humidity levels increased from 0 to 100 percent.<sup>25</sup>

Candidate standards being certified under Procedure P3 must be stored under constant temperature conditions between assays. A storage container for this application is described in the procedure.

When stored at a temperature other than the assay temperature, some permeation devices require an equilibration period at the assay temperature to reach thermal equilibrium and a stable, accurate

permeation rate. When transferred from a different storage temperature, thin-walled permeation devices should be maintained at the assay temperature with a fixed dilution flow rate for at least 48 hours before use or before certification. Temperature changes of  $>10\text{ }^{\circ}\text{C}$  may require equilibration periods of up to 15 days for  $\text{NO}_2$  permeation devices to attain a stable permeation rate.<sup>23,26</sup> Upon return to the original temperature, some devices may not return to the same permeation rate as before the temperature change. Other types of permeation devices may require longer equilibration periods. Observe any manufacturer's recommendations for equilibration and use.

#### **3.1.7.3 Equilibration of Newly Prepared Permeation Devices—**

A newly prepared permeation device must be equilibrated for at least 48 hours at the assay temperature before being assayed for the first time. The equilibration period may be 100 hours or longer for some permeation devices.<sup>26</sup> This period will vary as a function of the permeating compound, the material and the thickness of the permeating surface and the temperature.

#### **3.1.7.4 Certification Conditions for Permeation Device Calibration Standards—**

A standard will retain its certification only as long as 5 percent of the original liquid weight or a visible amount of liquid remains in it. A standard loses its certification if it is exposed for prolonged periods of time to excessive moisture or to temperatures greater than  $15\text{ }^{\circ}\text{C}$  above its certification temperature. A standard that loses its certification must be reassayed before it can be certified for further use.

### **3.1.8 Technical Variances**

Permeation device producers, standard users, and other analytical laboratories may petition the U.S. EPA for technical variances to the assay procedures in this protocol. A technical variance allows the use of a specific alternative assay procedure for candidate standards, which can be certified under this protocol. The petitioner must send a written request with a detailed description of the alternative assay procedure and supporting analytical data to Work Assignment Manager, EPA Traceability Protocol Project, U.S. EPA, Mail Code 47, Research Triangle Park, NC 27711. The supporting analytical data must demonstrate the equivalence of the alternative assay procedure with the procedures given in this protocol. Technical variances may also be given for alternative temperature ranges of certifying or storing permeation devices provided that supporting analytical data are provided with the written request.

Permeation device producers, standard users, and other analytical laboratories may petition the U.S. EPA to allow the assay and certification of permeation devices that contain gases or liquified gases other than  $\text{SO}_2$  and  $\text{NO}_2$ . The petitioner must send a written request with a detailed description of the permeation device and supporting analytical data to the EPA Work Assignment Manager at the address given above. The supporting analytical data must demonstrate that the permeation rate for the proposed device can be accurately determined, that only the specified compound is permeating, that the rate is stable over the lifetime of the device, and that the rate is not changed by temperature and humidity effects.

## **3.2 PROCEDURE P1: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATION STANDARDS REFERENCED TO A PERMEATION DEVICE REFERENCE STANDARD**

### **3.2.1 Applicability**

This procedure may be used to assay the permeation rate of a candidate  $\text{SO}_2$  or  $\text{NO}_2$  permeation device calibration standard, based on the permeation rate of a permeation device reference standard of the same pollutant compound, and to certify that the assayed permeation rate 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 concentrations from the two permeation devices for the

assay of the candidate device. This procedure may be used for the assay of multiple candidate standards during the same assay session. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards. This procedure may be used by permeation device producers, standard users, or other analytical laboratories.

### 3.2.2 Limitations

1. The permeation rate of the candidate standard may be greater than or lesser than the permeation rate of the reference standard. However, the diluted concentrations from both standards must lie within the well-characterized region of the analyzer's multipoint calibration (see Subsection 2.1.7.2). Additionally, the 95-percent uncertainty for the regression-predicted concentration of the diluted candidate standard must be 1.0 percent of the concentration of the diluted reference standard. This uncertainty is obtained from the statistical analysis of the multipoint calibration data using the spreadsheet described in Appendix A or using equivalent statistical techniques (e.g., the worksheet for linear relationships given in Chapter 5 of Reference 15). This criterion means that the uncertainty associated with the multipoint calibration determines the concentration range over which a diluted candidate standard may be assayed.
2. A quantitatively accurate flow measurement and dilution system is required.
3. A source of clean, dry zero gas is required.
4. This procedure is designed to assay the permeation rate of a candidate standard that is mounted in a specially designed assay dilution system; the procedure does not accommodate the certification of a candidate standard that is mounted in its own self-contained dilution/flow measurement system.

### 3.2.3 Assay Apparatus

Figure 3-1 illustrates the components and configuration of one possible design for the assay apparatus, including a common dilution system for both the reference and candidate standards. The configuration is designed to allow convenient routing of zero gas and diluted concentrations of the reference and candidate standards, in turn, to the analyzer for measurement, as selected by valves V1, V2, and V3. Three gas flow controllers (i.e., C1, C2, and C3) regulate the total dilution flow rates for both the reference and candidate permeation devices and the purge gas flow rate. These gas flow controllers may be needle valves, capillary tubes, thermal mass flow controllers, or other suitable devices. The flow rates must be controlled to within 1.0 percent variation during the assay.

The total dilution flow rate is measured by a single, common flowmeter (i.e., M1). Valve V1 directs a portion of the total dilution flow through one or the other of the two temperature-controlled permeation device chambers to sweep up the permeated pollutant gas. This sweep flow rate is monitored by an auxiliary flowmeter for each permeation device (i.e., M2 and M3). These auxiliary flowmeters need not be accurately calibrated, since only the total dilution flow measured by flowmeter M1 is used in the dilution calculation. Gas flow controllers C1 and C3 can be used to adjust and balance the flow rates of the two gas streams sweeping through the permeation device chambers. The permeation device that is not being analyzed receives a purge gas stream to avoid the buildup of high pollutant concentrations in the chamber. This purge gas flow is vented through valve V2 and is not measured by flowmeter M1.

The assay apparatus illustrated in Figure 3-1 may be modified by the addition of multiple candidate standard chambers. These chambers may be set to different temperatures.

If it is necessary to use different dilution flow rates for the candidate and reference permeation devices (see Subsection 3.2.6), separate flow controllers for the two permeation devices may be used for the two different flows. However, the same flowmeter should always be used to measure these two flow rates to minimize systematic flow measurement errors.

The mixing chamber combines the gas streams and should be designed to provide turbulence in the flow to ensure thorough mixing of the two gas streams. The diluted gas mixtures are routed to the analyzer through a union tee tube fitting, which vents excess gas flow. Normally, the excess gas is vented to the atmosphere without any obstructions in the tubing and the gas entering the analyzer is at near-atmospheric pressure. However, the excess gas can be routed through an uncalibrated rotameter by rotation of a three-way valve (i.e., V4). The rotameter is used to demonstrate that the total gas flow rate exceeds the sample flow rate of the analyzer and that no room air is being drawn in through the vent line (also see Subsection 3.1.4). Check the apparatus carefully for leaks and correct all leaks before use.

The mean temperatures of the reference standard chamber and the candidate standard chamber must be controlled to within 0.05 °C of the setpoint with a temperature stability of  $\pm 0.05$  °C. These temperatures must be measured with a NIST-traceable thermometer having a measurement uncertainty of  $\pm 0.05$  °C or less.



### 3.2.4 Pollutant Gas Analyzer

See Subsection 2.3.4. The pollutant gas analyzer must have a well-characterized calibration curve and a range capable of measuring the diluted concentrations of both the candidate and the reference standards. It must have good resolution, good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in the standards. A suitable analyzer with acceptable performance specifications may be selected from the list of EPA-designated reference and equivalent method analyzers.<sup>17</sup>

The analyzer should be connected to a high-precision data acquisition system (e.g., a strip chart recorder), which must produce an electronic or paper record for documentation of the analyzer responses obtained during the assay. Additionally, a digital panel meter with four-digit resolution, a digital voltmeter, data logger, or other data acquisition system must be used to obtain numerical values of the analyzer's response. More precise values will be obtained if these instruments have some data averaging capability. The assay record must be maintained for 3 years after the standard's certification date.

If the analyzer has not been in continuous operation, turn it on and allow it to stabilize (e.g., for at least 12 hours) before beginning any measurements.

### 3.2.5 Analyzer Calibration

#### 3.2.5.1 Multipoint Calibration—

See Subsections 2.1.7.2 and 2.1.7.4. Following completion of the multipoint calibration, the accuracy of the assay apparatus must be checked to verify that the error associated with the dilution is not excessive. This accuracy check involves the measurement of a diluted check standard. This check standard must be a permeation device that is traceable to a NIST SRM. It must have a certified permeation rate that is different from that of the reference standard used during the multipoint calibration. Information concerning this standard (e.g., permeation device identification number, certified permeation rate) must be recorded in the laboratory's records. The diluted concentration of the check standard must fall in the well-characterized region of the calibration curve.

Make three or more discrete measurements of the diluted check standard. "Discrete" means that the analyst must change the gas mixture being sampled by the analyzer between measurements. For example, the analyst might alternate between measurements of the diluted check standard and the zero gas. Record these measurements in the laboratory's records.

Next the analyst must verify that the dilution error is not excessive. For the diluted check standard measurements, calculate the relative difference (in percent) between the mean analyzer response and the corresponding response that is predicted from the multipoint calibration regression equation and the diluted check standard concentration. That is,

$$\text{Relative Difference} = 100 \left[ \frac{\text{Mean Analyzer Response} - \text{Predicted Response}}{\text{Predicted Response}} \right]$$

If the relative difference is greater than 1.0 percent, the dilution error is excessive. The analyst must investigate why the dilution error is excessive. The problem may be due to errors in the reference standard and check standard permeation rates, errors in the assay apparatus or to some other source. Assays may not be conducted until the relative difference for a subsequent accuracy check is 1.0 percent.

#### 3.2.5.2 Analyzer Range—

See Subsection 2.3.5.2.

### **3.2.5.3 Linearity—**

See Subsection 2.3.5.3.

### **3.2.5.4 Zero and Span Gas Checks—**

See Subsection 2.3.5.4.

## **3.2.6 Selection of Gas Dilution Flow Rates**

The dilution flow rates used for the reference and candidate standards should be selected carefully to provide diluted concentrations for both standards that fall in the well-characterized region of the analyzer's calibration curve. Potential errors in the assayed permeation rate due to dilution flow rate measurement error will be greatly reduced if the same dilution flow rates can be used for both standards. If the same dilution flow rates cannot be used for both standards, select different dilution flow rates for the candidate and reference devices to provide approximately equal diluted concentrations that fall in the well-characterized region. Additionally, the magnitude of the 95-percent confidence limits for the estimated concentration of the diluted candidate standard must be  $\pm 1$  percent of the concentration of the diluted reference standard.

## **3.2.7 Flowmeter Type and Flowmeter Calibration**

Flowmeter M1, as shown in Figure 3-1, measures in-line flow rates and does not operate at atmospheric pressure because of backpressure from downstream components. Also, this backpressure is variable, depending on the total dilution flow rate. Thus, the type of flowmeter used must compensate for the variable in-line pressure. Measurements from a pressure-sensitive flowmeter such as a rotameter or a wet test meter must be carefully corrected for the actual in-line pressure during the total dilution flow rate measurement.

Alternatively, the flow rates can be measured at the outlet of the dilution apparatus, with the excess gas flow vent temporarily plugged. In this case, a volume-type meter such as a wet test meter or a soap film flowmeter can be used, and flow measurements may be conveniently referenced to atmospheric pressure. Each flow rate must be measured independently while the other flow rate is set to zero. Great care must then be exercised to ensure that each measured flow rate remains constant between the time of measurement and the time of the assay.

The flowmeter used should be stable, repeatable, linear, and have good resolution. The flowmeter must not contaminate or react with the gas mixture passing through it. If possible, select flow rates or a flowmeter range such that the measured flow rates fall in the upper half of the flowmeter's range. The flowmeter should be carefully calibrated at several flow rates to prove linearity. The calibration should be accurate to  $\pm 1.0$  percent, referenced to an accurate flow or volume standard traceable to a NIST primary standard (see Subsection 3.1.2). The flowmeter calibration should be checked and recertified on a regular schedule (e.g., yearly). The recertification frequency is to be determined from stability information such as a chronological control chart of calibration data.

All volumetric flow rate measurements must be corrected or referenced to the same temperature and pressure conditions, such as EPA standard conditions (25 °C and 760 mm Hg) or the ambient temperature and pressure conditions prevailing in the laboratory during the assay. Measurements using wet test meters and soap bubble flowmeters also must be corrected for the saturation of gas stream with water vapor in the moist interiors of these flowmeters. The equation to correct the flow rate for temperature, pressure, and humidity effects is given below:

$$\text{Flow Rate} = \frac{\text{Volume}}{\text{Time}} \left( \frac{P_M - P_{WV}}{P_S} \right) \left( \frac{T_S}{T_M} \right)$$

where

- $P_M$  = measured barometric pressure (mm Hg);
- $P_{WV}$  = partial pressure of water vapor (mm Hg);
- $P_S$  = standard pressure (mm Hg);
- $T_S$  = standard temperature (298.2 K);
- $T_M$  = measured ambient temperature (273.2 + °C).

Measurement of both dilution flow rates with the same flowmeter tends to reduce systematic flow measurement error. Note particularly that flow measurement error is greatly reduced if the same dilution flow rates can be used for both the reference and candidate standards.

### 3.2.8 Permeation Devices

#### 3.2.8.1 Candidate Standard—

See Subsections 3.1.7 and 3.2.2. Follow the manufacturer's instructions for equilibration and for use of the candidate standard and for selecting the temperature at which it is to be assayed and certified. The candidate standard should be assayed at the same temperature at which it will be subsequently used. The mean operating temperature of the candidate standard chamber must be controlled to within 0.05 °C of the setpoint with a temperature stability of ±0.05 °C. This temperature must be measured with a NIST-traceable thermometer with a measurement uncertainty of ±0.05 °C or less (see Subsection 3.1.2).

#### 3.2.8.2 Reference Standard—

See Subsections 3.1.2, 3.1.7.1, 3.1.7.2, and 3.2.2. Follow NIST's instructions for equilibration and use of the SRM reference standard and for selecting an operating temperature within its certified range. The mean operating temperature of the reference standard chamber must be controlled to within 0.05 °C of the setpoint with a temperature stability of ±0.05 °C. This temperature must be measured with a NIST-traceable thermometer with a measurement uncertainty of ±0.05 °C or less.

#### 3.2.8.3 Zero Gas—

See Subsection 2.1.8. Use the same zero gas for dilution of both the candidate and reference standards.

### 3.2.9 Assay Procedure

1. Verify that the assay apparatus is properly configured as shown in Figure 3-1 and described in Subsection 3.2.3. Inspect the analyzer to verify that it appears to be operating normally and that all controls are set to their expected values. Record these control values in the laboratory's records.
2. Determine and establish the operating temperatures for the reference and candidate standards in their respective temperature-controlled chambers. Install the standards and, with zero gas flowing over both standards, allow ample time for the standards to equilibrate (see Subsection 3.1.7.2). Record the temperatures in the laboratory's records.

3. Verify that flowmeter M1 is properly calibrated (see Subsection 3.2.7).
4. Verify that a multipoint calibration of the analyzer has been performed within 1 month prior to the assay date (see Subsections 2.1.7.2, 2.1.7.5, and 2.3.4). Additionally, verify that the zero and span gas checks indicate that the analyzer is in calibration (see Subsection 2.3.5.4).
5. Determine and establish the dilution flow rates and diluted concentrations for the reference and candidate standards that will be used for the assay (see Subsections 3.2.6, 3.2.7, and 3.2.5.2). Use an estimated permeation rate for the candidate standard in these calculations. Calculate the diluted standard concentrations (in ppm) using the following equation:

$$\text{Diluted Standard Conc.} = \left[ 10^{-3} \right] \left[ \frac{\text{MV}}{\text{MW}} \right] \left[ \frac{\text{Permeation Rate}}{\text{Dilution Flow Rate}} \right]$$

where

MV = Molar volume of the dilution gas (liters/mole);

$$= (0.08206) T_m$$

MW = Molecular weight of the dilution gas (grams/mole); permeation rate is given in nanograms/minute; and dilution flow rate is given in liters/minute.

Ensure that the diluted candidate and reference standard concentrations are within the well-characterized region of the analyzer's calibration curve (see Subsection 2.3.2). Also check that both dilution flow rates will provide enough flow for the analyzer, with sufficient excess to ensure that no ambient air will be drawn into the vent line, and without increasing the pressure of the sample delivered to the analyzer. If possible, use the same dilution flow rate for both standards. Record the measured flow rates in the laboratory's records.

6. In succession, measure the zero gas, the diluted reference standard and the diluted candidate standard using the analyzer. Use valves V1, V2, and V3 to select each of the three gas mixtures for measurement. For each measurement, adjust the flow rates, if necessary, to those determined in step 5, and allow ample time for the analyzer to achieve a stable reading. If the reading for each measurement is not stable, the precision of the measurements will decline and the candidate standard might not be certifiable under this protocol. Record the analyzer response for each measurement, using the same response units (e.g., volts, millivolts, percent of scale, etc.) as was used for the multipoint calibration. At this point, do not convert the data into concentration values using the calibration equation. Do not perform any mathematical transformations of the data. These steps will be done later. Do not make any zero control, span control, or other adjustments to the analyzer during this set of measurements. Record these analyzer responses in the laboratory's records.

The analyst may assay multiple candidate standards during the same assay session. For example, a single set of measurements may involve a zero gas, a diluted reference standard, and three diluted candidate standards. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards. The analyst should be aware that the effect of any short-term calibration drift will be greater when multiple candidate standards are assayed. This greater effect is due to the longer period of time between reference standard measurements. Unacceptable uncertainties of the estimated

concentrations for the diluted candidate standards may occur as a result of the longer assay session.

7. Conduct at least two additional sets of measurements, as described in step 6 above. However, for these subsequent sets of measurements, change the order of the three measurements (e.g., measure the reference standard, zero gas, and candidate standard for the second set and measure the zero gas, candidate standard, and reference standard for the third set, etc.). Changing the order that the gas mixtures are measured helps the analyst to discover any effect that one measurement has on subsequent measurements. The number of sets of measurements will have been determined during the analysis of the multipoint calibration data such that the 95-percent uncertainty for the regression-predicted concentration is 1 percent of the concentration of the reference standard.
8. If any one or more of the measurements of a set of measurements is invalid or abnormal for any reason, discard all three measurements and repeat the set of measurements. Such measurements may be discarded if the analyst can demonstrate that the experimental conditions were inappropriate during these measurements. Data cannot be discarded just because they appear to be outliers, but may be discarded if they satisfy statistical criteria for testing outliers.<sup>16</sup> The analyst must record any discarded data and a brief explanation about why the data were discarded in the laboratory's records.
9. The spreadsheet described in Appendix A or equivalent statistical techniques must be used to calculate an estimated concentration and a 95-percent uncertainty for the diluted candidate standard based on data from the assay measurements and from the multipoint calibration. The use of both sets of data in the statistical analysis produces an estimated concentration with smaller uncertainty while correcting for any minor calibration drift that may have occurred since the multipoint calibration. Record the estimated concentration and the 95-percent uncertainty in the laboratory's records.

The spreadsheet also calculated the percentage of the uncertainty that is due to the multipoint calibration. This percentage is needed for the total uncertainty calculations when two or more assays fall under the same multipoint calibration. Record this value in the laboratory's records.

The analyst should investigate any of the measurements that appear to be outliers. Such data may be discarded if the analyst can demonstrate that the experimental conditions were inappropriate during these measurements. Data cannot be discarded just because they appear to be outliers, but may be discarded if they satisfy statistical criteria for testing outliers. The analyst must record any discarded data as well as a brief summary of the investigation in the laboratory's records.

10. If the multipoint calibration data and the assay data underwent any mathematical transformations before their statistical analysis, the analyst must perform to reverse transformations for the estimated concentration and the 95-percent uncertainty. Record the transformed values in the laboratory's records.
11. Finally, calculate the certified permeation rate (in nanograms/minute) and uncertainty for the candidate standard using the equations below:

$$\text{Certified Permeation Rate} = \left[ 10^3 \right] \left[ \frac{\text{MW}}{\text{MV}} \right] \left[ \begin{array}{c} \text{Diluted Standard} \\ \text{Conc.} \end{array} \right] \left[ \begin{array}{c} \text{Dilution Flow} \\ \text{Rate} \end{array} \right]$$

$$\text{Uncertainty of Permeation Rate} = \left[ 10^3 \right] \left[ \frac{\text{MW}}{\text{MV}} \right] \left[ \begin{array}{c} 95\text{-Percent} \\ \text{Uncertainty} \end{array} \right] \left[ \begin{array}{c} \text{Dilution Flow} \\ \text{Rate} \end{array} \right]$$

### 3.2.10 Equilibration Test for Newly Prepared Permeation Devices

A permeation device that has not been previously assayed must be tested for a stable permeation rate as follows: Reassay the permeation rate at least 24 hours after the first assay and compare the two assayed concentrations. The spreadsheet described in Appendix C or equivalent statistical techniques must be used to evaluate the stability of the permeation rate by comparison of the confidence limits from the two assays. If the confidence intervals overlap, the permeation rate can be considered to be stable and the candidate standard may be certified for use. Otherwise, equilibrate the device longer at the operating temperature and repeat the test, using the second and third assays as if they were the first and second. This process may be repeated until the rate stabilizes. Permeation devices that are not stable may not be used for calibration or audit purposes. Candidate standards that fail the initial and the repeat stability tests are unstable and are disqualified for further use under this protocol.

### 3.2.11 Certification Documentation

See Subsections 3.1.5 and 3.1.6.

### 3.2.12 Recertification Requirements

See Subsection 3.1.7.3.

## 3.3 PROCEDURE P2: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATION STANDARDS REFERENCED TO A COMPRESSED GAS REFERENCE STANDARD

### 3.3.1 Applicability

This procedure may be used to assay the permeation rate of a candidate SO<sub>2</sub> and NO<sub>2</sub> permeation device calibration standard, based on the concentration of a compressed gas reference standard of the same pollutant compound, and to certify that the assayed permeation rate 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 concentrations from the permeation device calibration standard with quantitatively diluted concentrations from the compressed gas reference standard. This procedure may be used for the assay of multiple candidate standards during the same assay session. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards. This procedure may be used by permeation device producers, standard users or other analytical laboratories.

### 3.3.2 Limitations

1. The concentration of the diluted candidate standard may be greater than or less than the concentration of the diluted reference standard. However, the diluted concentrations from both standards must lie within the well-characterized region of the analyzer's calibration curve (see Subsection 2.1.7.2). Additionally, the 95-percent uncertainty for the regression-predicted concentration of the diluted candidate standard must be 1.0 percent of the concentration of the diluted reference standard. This uncertainty is obtained from the statistical analysis of the multipoint calibration data using the spreadsheet described in Appendix A or using equivalent statistical techniques (e.g., the worksheet for linear relationships given in Chapter 5 of Reference 15). This criterion means that the uncertainty associated with the multipoint calibration determines the concentration range over which a diluted candidate standard may be assayed.
2. A quantitatively accurate dilution and flow measurement system is required.
3. A source of clean, dry zero gas is required.
4. This procedure is designed to assay the permeation rate of a candidate standard that is mounted in a specially designed assay dilution system. The procedure does not accommodate the certification of a candidate standard that is mounted in its own self-contained dilution/flow measurement system.

### **3.3.3 Assay Apparatus**

Figure 3-2 illustrates the components and configuration of one possible design for the assay apparatus, including a common dilution system for both the reference and candidate standards.



The configuration is designed to allow convenient routing of zero gas and diluted concentrations of the reference standard and the candidate standard, in turn, to the analyzer for measurement, as selected by valves V1, V2, and V3. Three gas flow controllers (i.e., C1, C2, and C3) regulate the total dilution flow rate for the candidate standard, the purge gas flow rate, and the reference standard flow rate. These gas flow controllers may be needle valves, capillary tubes, thermal mass flow controllers, or other suitable devices. The flow rates should be controlled to within 1.0 percent variation during the assay. The dilution flow rates for the reference and candidate standards is measured by a single, common flowmeter (i.e., M1). The reference standard and purge gas flow rates may be measured at the vent port of valve V2 or by flowmeters M2 and M3 that are mounted in the two gas streams.

When the candidate standard is being measured, valve V1 directs a portion of the total dilution flow through the candidate standard chamber. This sweep flow rate is regulated by gas flow controller C1 and is measured by gas flowmeter M2. This flowmeter need not be accurately calibrated because only the total dilution flow rate, measured by flowmeter M1, is used in the dilution calculations. When the reference standard is being measured, valve V1 directs the purge gas through the candidate standard chamber. The purge gas prevents the buildup of high pollutant concentrations in the chamber. It is vented through valve V2 and is not measured by flowmeter M1.

The assay apparatus illustrated in Figure 3-2 may be modified by the addition of multiple candidate standard chambers. These chambers may be set to different temperatures.

If it is necessary to use different dilution flow rates for the reference standard and the candidate standard (see Subsection 3.2.6), separate flow controllers for the two dilution flow rates may be used. However, the same flowmeter should be used to measure both dilution flow rates to help reduce systematic flow measurement errors.

The mixing chamber combines the gas streams and should be designed to provide turbulence in the flow to ensure thorough mixing of the two gas streams. The diluted gas mixtures are routed to the analyzer through a union tee tube fitting, which vents excess gas flow. Normally, the excess gas is vented to the atmosphere without any obstructions in the tubing and the gas entering the analyzer is at near-atmospheric pressure. However, the excess gas can be routed through an uncalibrated rotameter by rotation of a three-way valve (i.e., V4). The rotameter is used to demonstrate that the total gas flow rate exceeds the sample flow rate of the analyzer and that no room air is being drawn in through the vent line (also see Subsection 3.1.4). Check the apparatus carefully for leaks and correct all leaks before use.

The mean temperature of the candidate standard chamber must be controlled to within 0.05 °C of the setpoint with a temperature stability of  $\pm 0.05$  °C. This temperature must be measured with a NIST-traceable thermometer having a measurement uncertainty of not more than 0.05 °C.

### **3.3.4 Pollutant Gas Analyzer**

See Subsection 2.3.4. The pollutant gas analyzer must have a well-characterized calibration curve and a range capable of measuring the diluted concentrations of both the candidate and reference standards. It must have good resolution, good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in the standards. A suitable analyzer with acceptable performance specifications may be selected from the list of EPA-designated reference and equivalent method analyzers.<sup>17</sup> If the balance gas of the reference standard must be different from the zero gas used for dilution (e.g., air versus nitrogen or different proportions of oxygen), either a high dilution ratio (i.e., at least 50 parts zero gas to 1 part standard) should be used, or the analyzer must be proven to be not sensitive to differences in the balance gas composition. The latter may be

demonstrated by showing no difference in an analyzer's response when measuring a calibration standard that has been diluted with identical flow rates of the different balance gases.

The analyzer should be connected to a high-precision data acquisition system (e.g., a strip chart recorder) which must produce an electronic or paper record of the analyzer response during the assay. Additionally, a digital panel meter with four-digit resolution, a digital voltmeter, data logger, or other data acquisition system must be used to obtain numerical values of the analyzer's response. More precise values will be obtained if these instruments have some data averaging capability. The assay record must be maintained for 3 years after the standard's certification date.

If the analyzer has not been in continuous operation, turn it on and allow it to stabilize (e.g., for at least 12 hours) before beginning any measurements.

### **3.3.5 Analyzer Calibration**

#### **3.3.5.1 Multipoint Calibration—**

See Subsections 2.1.7.2 and 2.1.7.4. Following completion of the multipoint calibration, the accuracy of the assay apparatus must be checked to verify that the error associated with the dilution is not excessive. This accuracy check involves the measurement of an undiluted or diluted check standard. The check standard must be a NIST SRM, an SRM-equivalent PRM, an NTRM, or a GMIS as specified in Subsection 2.1.2. It must have a certified concentration that is different from that of the reference standard used in the multipoint calibration. Information concerning this standard (e.g., cylinder identification number, certified concentration) must be recorded in the laboratory's records.

If an undiluted check standard is used, its concentration must fall in the well-characterized region of the calibration curve. If a diluted check standard is used, the diluted concentration must fall in the well-characterized region.

Make three or more discrete measurements of the undiluted or diluted check standard. "Discrete" means that the analyst must change the gas mixture being sampled by the analyzer between measurements. For example, the analyst might alternate between measurements of the check standard and the zero gas. Record these measurements in the laboratory's records.

Next the analyst must verify that the dilution error is not excessive. For the check standard measurements, calculate the relative difference (in percent) between the mean analyzer response and the corresponding response that is predicted from the multipoint calibration regression equation and the undiluted or diluted check standard concentration. That is,

$$\text{Relative Difference} = 100 \left[ \frac{\text{Mean Analyzer Response} - \text{Predicted Response}}{\text{Predicted Response}} \right]$$

If the relative difference is >1.0 percent, the dilution error is considered to be excessive. The analyst must investigate why the relative difference is excessive. The program may be due to errors in the reference standard and check standard concentrations, errors in assay apparatus or to some other source. Assays may not be conducted until the relative difference for a subsequent accuracy check is 1.0 percent.

#### **3.3.5.2 Analyzer Range—**

See Subsection 2.3.5.2.

#### **3.3.5.3 Linearity—**

See Subsection 2.3.5.3.

#### **3.3.5.4 Zero and Span Gas Checks—**

See Subsection 2.3.5.4.

#### **3.3.6 Selection of Gas Dilution Flow Rates**

The dilution flow rates used for the reference standard and the candidate standard should be selected carefully to provide diluted concentrations for both standards that fall in the well-characterized region of the analyzer's calibration curve. Potential errors in the assayed permeation rate due to dilution flow rate measurement error will be reduced if the same dilution flow rates can be used for both the reference and candidate standards. This should be feasible by appropriate selection of the reference standard flow rate. Select a combination of reference standard flow rate and dilution flow rate that produces approximately equal diluted reference standard and candidate standard concentrations that fall in the well-characterized region of the analyzer's calibration curve. Additionally, the magnitude of the 95-percent confidence limits for the estimated concentration of the diluted candidate standard must be  $\pm 1$  percent of the concentration of the diluted reference standard.

#### **3.3.7 Flowmeter Type and Flowmeter Calibration**

Flowmeters M1 and M3, shown in Figure 3-2, measure in-line flow rates and do not operate at atmospheric pressure because of backpressure from downstream components. Also, this backpressure is variable, depending on the total dilution and reference standard flow rates. Thus, the flowmeters must compensate for the variable in-line pressure. Thermal mass flowmeters do not need to be corrected for pressure effects. Measurements from pressure-sensitive flowmeters such as rotameters or wet test meters must be carefully corrected for the actual in-line pressure during the flow rate measurements.

Alternatively, the flow rates can be measured at the outlet of the dilution apparatus, with the excess gas flow vent temporarily plugged. In this case, a volume-type meter such as a wet test meter or a soap film flowmeter can be used, and flow measurements may be conveniently referenced to atmospheric pressure. Each flow rate must be measured independently while the other flow rate is set to zero. Great care must be exercised to ensure that each measured flow rate remains constant when combined with the other flow rate and between the time of measurement and the time of the assay.

The flowmeters used should be stable, repeatable, linear, and have good resolution. The flowmeters must not contaminate or react with the gas mixture passing through them. If possible, select flow rates or flowmeter ranges such that the measured flow rates fall in the upper half of the flowmeters' ranges. The flowmeters should be carefully calibrated at several flow rates to prove linearity. The calibration of the zero gas flowmeter should be accurate to  $\pm 1.0$  percent, referenced to an accurate flow or volume standard traceable to a NIST primary standard (see Subsection 3.1.2). This flowmeter calibration should be checked and recertified on a regular schedule (e.g., yearly). The recertification frequency is to be determined from stability information such as a chronological control chart of calibration data.

It is desirable to measure both dilution flow rates with the same flowmeter (i.e., M1). This practice reduces measurement errors associated with the use of multiple flowmeters. Note that the impact of any flow measurement error is reduced if the same dilution ratio can be used for both candidate standard and reference standard measurements.

All volumetric flow-rate measurements must be corrected or referenced to the same temperature and pressure conditions, such as EPA-standard conditions (i.e., 760 millimeters of mercury (mm Hg) and 25 °C) or the ambient temperature and pressure conditions prevailing in the laboratory during the assay. Measurements using wet test meters and soap bubble flowmeters also must be corrected for the saturation

of the gas stream with water vapor in the moist interiors of these flowmeters. The equation to correct the flow rate for temperature, pressure, and humidity effects is given below:

$$\text{Flow Rate} = \frac{\text{Volume}}{\text{Time}} \left( \frac{P_M - P_{WV}}{P_S} \right) \left( \frac{T_S}{T_M} \right)$$

where

- $P_M$  = measured barometric pressure (mm Hg);
- $P_{WV}$  = partial pressure of water vapor (mm Hg);
- $P_S$  = standard pressure (mm Hg);
- $T_S$  = standard temperature (298.2 K); and
- $T_M$  = measured ambient temperature (273.2 + °C).

### 3.3.8 Candidate Standard

See Subsections 3.1.7 and 3.2.2. Follow the manufacturer's instructions for equilibration and for use of the candidate standard and for selecting the temperature at which it is to be assayed and certified. The candidate standard should be assayed at the same temperature at which it will be subsequently used. The mean operating temperature of the candidate standard chamber must be controlled to within 0.05 °C of the setpoint with a temperature stability of ±0.05 °C. This temperature must be measured with a NIST-traceable thermometer with a measurement uncertainty ±0.05 °C or less (see Subsection 3.1.2).

### 3.3.9 Reference Standard

See Subsections 2.1.2, 2.1.6.4, 2.3.2, 2.3.6, and 3.1.2.

### 3.3.10 Zero Gas

See Subsection 2.1.8. If possible, the zero gas should be the same as the balance gas of the reference standard.

### 3.3.11 Assay Procedure

1. Verify that the assay apparatus is properly configured as shown in Figure 3-2 and described in Subsection 3.3.3. Inspect the analyzer to verify that it appears to be operating normally and that all controls are set to their expected values. Record these control values in the laboratory's records.
2. Determine and establish the operating temperature for the candidate standard in its temperature-controlled chamber. Install the candidate standard, start the purge gas flow, and allow ample time for the device to equilibrate (see Subsection 3.1.7.2). Record the temperature in the laboratory's records.
3. Verify that the flowmeters are properly calibrated (see Subsection 3.3.7).
4. Verify that a multipoint calibration of the analyzer has been performed within 1 month prior to the assay date (see Subsections 2.1.7.2, 2.1.7.5, and 2.3.4). Additionally, verify that

the zero and span gas checks indicate that the analyzer is in calibration (see Subsection 2.3.5.4).

5. Determine and establish the reference standard flow rate and the dilution flow rates and diluted concentrations for the reference standard and the candidate standard that will be used for the assay (see Subsections 2.3.5.2 and 3.3.6). Ensure that the diluted reference standard and diluted candidate standards concentrations are within the well-characterized region of the analyzer's calibration curve (see Subsection 2.3.2). Also check that both dilution flow rates will provide enough flow for the analyzer, with sufficient excess to ensure that no ambient air will be drawn into the vent line. If possible, use the same dilution flow rate for both the reference standard and the candidate standard. Also adjust the flow rate of the portion of the dilution flow that passes over the candidate standard (i.e., flow controller C3), and adjust the purge flow rate (i.e., flow controller C2) to approximately the same value.

Calculate the diluted reference standard concentration using the following equation:

$$\text{Diluted Standard Conc.} = \left[ \frac{(\text{Undiluted Standard Conc.}) (\text{Standard Flow Rate})}{(\text{Standard Flow Rate} + \text{Zero Gas Flow Rate})} \right]$$

Calculate the diluted candidate standard concentration (in ppm) using the following equation:

$$\text{Diluted Standard Conc.} = \left[ 10^{-3} \right] \left[ \frac{\text{MV}}{\text{MW}} \right] \left[ \frac{\text{Permeation Rate}}{\text{Dilution Flow Rate}} \right]$$

where

MV = Molar volume of the dilution gas (liters/mole);

$$= (0.08206) T_m$$

MW = Molecular weight of the dilution gas (grams/mole); permeation rate is given in nanograms/minute; and dilution flow rate is given in liters/minute.

Use an estimated permeation rate for the candidate standard in this calculation.

Record the measured flow rates and the undiluted and diluted reference standard concentrations in the laboratory's records.

6. In succession, measure the zero gas, the diluted reference standard and the diluted candidate standard using the analyzer. Use valves V1, V2, and V3 to select each of the three gas mixtures for measurement. For each measurement, adjust the flow rates, if necessary, to those determined in step 5, and allow ample time for the analyzer to achieve a stable reading. If the reading for each measurement is not stable, the precision of the measurements will decline and the candidate standard might not be certifiable under this protocol. Record the analyzer response for each measurement, using the same response units (e.g., volts, millivolts, percent of scale, etc.) as was used for the multipoint calibration. At this point, do not convert the data into concentration values using the calibration equation. Do

not perform any mathematical transformations of the data. These steps will be done later. Do not make any zero control, span control, or other adjustments to the analyzer during this set of measurements. Record these analyzer responses in the laboratory's records.

The analyst may assay multiple candidate standards during the same assay session. For example, a single set of measurements may involve a zero gas, a diluted reference standard, and three diluted candidate standards. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards. The analyst should be aware that the effect of any short-term calibration drift will be greater when multiple candidate standards are assayed. This greater effect is due to the longer period of time between reference standard measurements. Unacceptable uncertainties of the estimated concentrations for the diluted candidate standards may occur as a result of the longer assay session.

7. Conduct at least two additional sets of measurements, as described in step 6 above. However, for these subsequent sets of measurements, change the order of the three measurements (e.g., measure the reference standard, zero gas, and candidate standard for the second set and measure the zero gas, candidate standard, and reference standard for the third set, etc.). Changing the order that the gas mixtures are measured helps the analyst to discover any effect that one measurement has on subsequent measurements. The number of sets of measurements will have been determined during the analysis of the multipoint calibration data such that the 95-percent uncertainty of the regression-predicted concentration of the candidate standard is 1 percent of the concentration of the reference standard.
8. If any one or more of the measurements of a set of measurements is invalid or abnormal for any reason, discard all three measurements and repeat the set of measurements. Such measurements may be discarded if the analyst can demonstrate that the experimental conditions were inappropriate during these measurements. Data cannot be discarded just because they appear to be outliers, but may be discarded if they satisfy statistical criteria for testing outliers.<sup>16</sup> The analyst must record any discarded data and a brief explanation about why the data were discarded in the laboratory's records.
9. The spreadsheet described in Appendix A or equivalent statistical techniques must be used to calculate an estimated concentration and a 95-percent uncertainty for the diluted candidate standard based on data from the assay measurements and from the multipoint calibration. The use of both sets of data in the statistical analysis produces an estimated concentration with smaller uncertainty while correcting for any minor calibration drift that may have occurred since the multipoint calibration. Record the estimated concentration and the 95-percent uncertainty in the laboratory's records.

The spreadsheet also calculated the percentage of the uncertainty that is due to the multipoint calibration. This percentage is needed for the total uncertainty calculations when two or more assays fall under the same multipoint calibration. Record this value in the laboratory's records.

The analyst should investigate any of the measurements that appear to be outliers. Such data may be discarded if the analyst can demonstrate that the experimental conditions were inappropriate during these measurements. Data cannot be discarded just because they appear to be outliers, but may be discarded if they satisfy statistical criteria for testing outliers. The analyst must record any discarded as well as a brief summary of the investigation in the laboratory's records.

10. If the multipoint calibration data and the assay data underwent any mathematical transformations before their statistical analysis, the analyst must perform to reverse transformations for the estimated concentration and the 95-percent uncertainty. Record the transformed values in the laboratory's records.
11. Finally, calculate the certified permeation rate (in nanograms/minute) and uncertainty for the candidate standard using the equations below:

$$\text{Certified Permeation Rate} = \left[ 10^3 \right] \left[ \frac{\text{MW}}{\text{MV}} \right] \left[ \begin{array}{c} \text{Diluted Standard} \\ \text{Conc.} \end{array} \right] \left[ \begin{array}{c} \text{Dilution Flow} \\ \text{Rate} \end{array} \right]$$

$$\text{Uncertainty of Permeation Rate} = \left[ 10^3 \right] \left[ \frac{\text{MW}}{\text{MV}} \right] \left[ \begin{array}{c} 95\text{-Percent} \\ \text{Uncertainty} \end{array} \right] \left[ \begin{array}{c} \text{Dilution Flow} \\ \text{Rate} \end{array} \right]$$

### 3.3.12 Equilibration Test for Newly Prepared Permeation Devices

A permeation device that has not been previously assayed must be tested for a stable permeation rate as follows: Reassay the permeation rate at least 24 hours after the first assay and compare the two assayed concentrations. The spreadsheet described in Appendix C or equivalent statistical techniques must be used to evaluate the stability of the permeation rate by comparison of the confidence limits from the two assays. If the confidence intervals overlap, the permeation rate can be considered to be stable and the candidate standard may be certified for use. Otherwise, equilibrate the device longer at the operating temperature and repeat the test, using the second and third assays as if they were the first and second. This process may be repeated until the rate stabilizes. Permeation devices that are not stable may not be used for calibration or audit purposes. Candidate standards that fail the initial and the repeat stability tests are unstable and are disqualified for further use under this protocol.

### 3.3.13 Certification Documentation

See Subsections 3.1.5 and 3.1.6.

### 3.3.14 Recertification Requirements

See Subsection 3.1.7.3.

## 3.4 PROCEDURE P3: ASSAY AND CERTIFICATION OF PERMEATION DEVICE CALIBRATION STANDARDS REFERENCED TO A MASS REFERENCE STANDARD

### 3.4.1 Applicability

This procedure may be used to assay the permeation rate of a candidate SO<sub>2</sub> or NO<sub>2</sub> permeation device calibration standard based on mass reference standards, and to certify that the assayed permeation rate is traceable to the reference standard. The procedure employs an analytical balance to measure the weight loss in the candidate standard. It may be used for the assay of multiple candidate standards during the same assay session. Criteria that apply to the assay of one candidate standard apply to the assay of

multiple candidate standards. This procedure may be used by permeation device producers, standard users, or other analytical laboratories.

### 3.4.2 Limitations

1. This procedure is intended only for the assay of candidate standards containing SO<sub>2</sub> or NO<sub>2</sub>. These liquid compounds must be anhydrous grade (minimum purity 99.99 percent) or phosphorous pentoxide-dried commercial purity grade (minimum purity 99.5 percent).
2. An accurate analytical balance with a NIST-traceable calibration is required to weigh the candidate standard.
3. A temperature-controlled chamber for maintaining the candidate standard at a constant, NIST-traceable temperature between weight measurements is required.
4. A source of clean, dry zero gas is required.

### 3.4.3 Assay Apparatus

#### 3.4.3.1 Analytical Balance—

Choose a balance with adequate vibration-stabilization control and appropriate specifications for total weighing capacity, accuracy, precision, and readability. The balance should be chosen such that the manufacturer's specified uncertainty (i.e., three times the standard deviation or "reproducibility") of the balance divided by the weight of the candidate standard does not exceed 0.001. The balance must be calibrated annually using NIST-traceable mass reference standards by the manufacturer or a manufacturer's representative (see Subsection 3.1.2).

If possible, locate the balance in a climate-controlled, draft-free room, preferably dedicated to the use of balances. If this is not possible, the general guidelines listed below should be followed to control environmental factors that may affect balance performance:

- ! Locate the balance away from potential sources of drafts such as doors, windows, aisles with frequent traffic, ventilation ducts, and equipment with fans or moving parts.
- ! Locate the balance out of direct sunlight and away from local heating or cooling sources such as open flames, hot plates, water baths, ventilation ducts, windows, and heat-producing lamps.
- ! Locate the balance on a sturdy base (ideally, a stone weighing table) and away from any equipment that produces vibrations. If this is not possible, isolate the balance from such equipment by placing a stabilizing slab under the balance or composite damping-pads under the balance legs.
- ! Ensure that the balance-support is sufficiently level to permit leveling of the balance according to the manufacturer's instructions.

#### 3.4.3.2 Temperature-Controlled Chamber—

A temperature-controlled chamber is required for storing the candidate standard between weighings. One possible design for the chamber is depicted in Figure 3-3.<sup>23</sup> Clean, dry zero gas enters the chamber at the bottom after passing through the heat exchanger tubing (i.e., several turns of copper tubing). The zero gas' flow rate must be sufficient to purge the chamber thoroughly. The chamber and the heat exchanger are immersed in a thermostatted bath to the level shown in the figure. The bath must

control the mean temperature of the chamber to within 0.05 °C of the setpoint with a temperature stability of  $\pm 0.05$  °C. The temperature of the bath or the chamber must be measured and recorded in the laboratory's records on at least a daily basis. A NIST-traceable, liquid-in-glass thermometer or a temperature-sensing device must be used for this measurement (see Subsection 3.1.2). A temperature-sensing device must be calibrated annually using NIST-traceable temperature reference standards and must have an uncertainty similar to that of these reference standards. The output of a temperature-sensing device may be recorded by a strip chart recorder, data logger, or other data acquisition system.

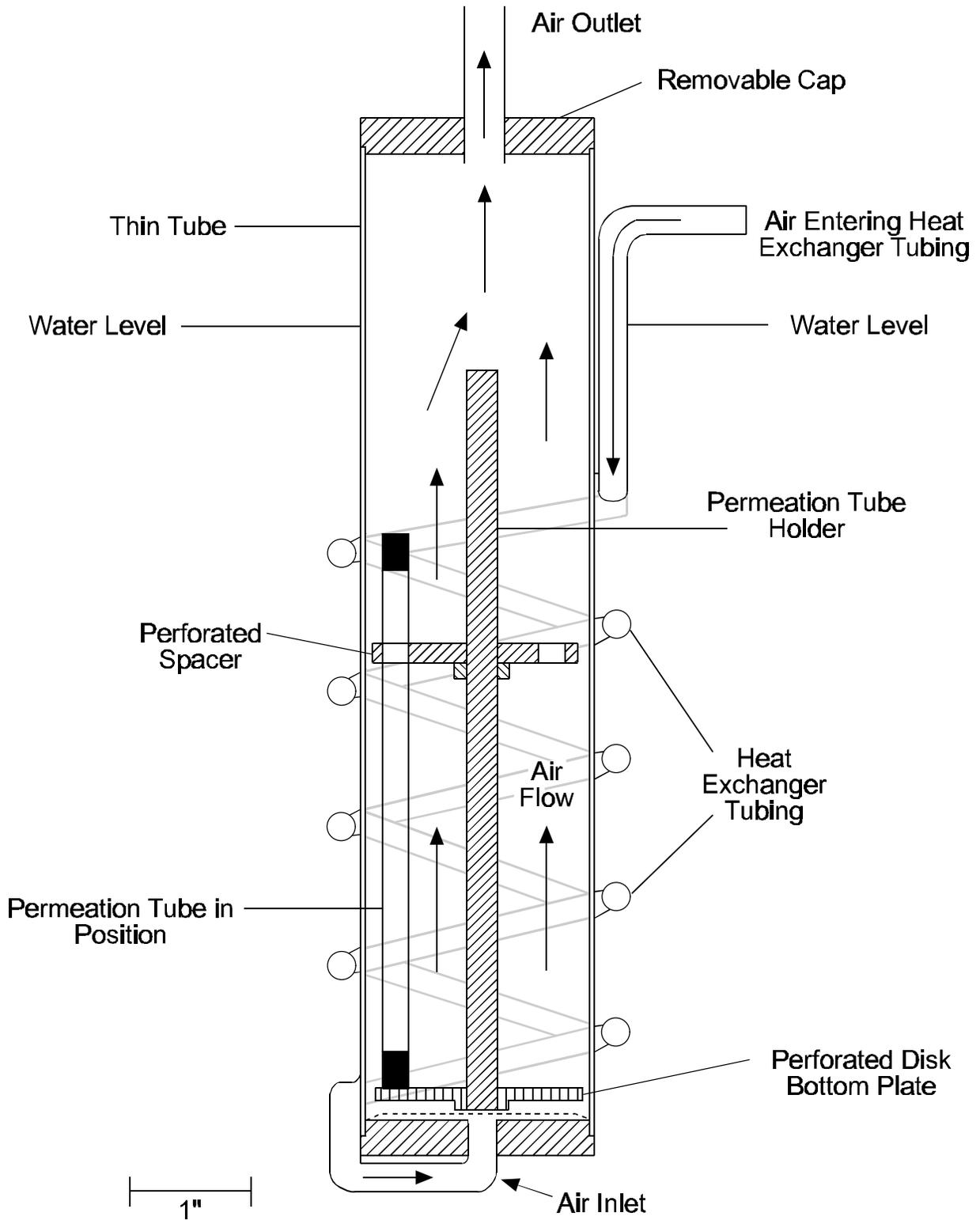


Figure 3-3. Chamber for maintaining permeation tubes at constant temperature.<sup>23</sup>

### 3.4.3.3 Electrostatic Charge Neutralization—

Electrostatic charge buildup will prevent an analytical balance from operating properly. Static charge is the accumulation of electrical charges on the surface of a nonconductive material, which could be the permeation device or part of the analytical balance. Common symptoms of this problem include noisy readout, drift, and sudden readout shifts.

To reduce static charge within the balance, it may be necessary to place a radioactive antistatic strip containing a very small amount (i.e., 500 picocuries) of Polonium-210 ( $\text{Po}^{210}$ ) in the weighing chamber. It may also be necessary to put each permeation device on an antistatic strip before it is weighed.  $\text{Po}^{210}$  antistatic strips are used to reduce electrostatic buildup in the analytical balance's weighing chamber and on individual permeation devices by charge neutralization. They will neutralize electrostatic charges on items placed within an inch of them. These antistatic strips are safe, commonly available, and very inexpensive.  $\text{Po}^{210}$  has a half-life of 138 days. Change the antistatic strips semiannually and dispose of the old strips according to the manufacturer's recommendations.

Antistatic solutions are available for coating (and recoating at appropriate and relatively infrequent intervals) the interior and exterior nonmetallic surfaces of the chamber. This coating facilitates the draining of electrostatic charges from these surfaces to a common electrical ground to which the metallic conductive surfaces are connected. Earth-grounded conductive mats placed on the weighing table surface and under the analyst's shoes are used to reduce electrostatic charge buildup. Do not assume that the electrical grounding of the analytical balance eliminates all electrostatic buildup because the ground may not be perfect.

Even though a permeation device's weight might stabilize within 60 seconds and no weight drift is observed during that period, the balance may still be influenced by electrostatic charge buildup. It may still be necessary to repeat the neutralization procedure and to use antistatic strips inside the weighing chamber. One may reduce the effect of electrostatic buildup on permeation devices by putting them in an aluminum foil boat on the balance pan during weighings.

Charge neutralization times may need to be longer than 60 seconds. Electrostatic charge buildup becomes greater as the air becomes drier. A 60-second neutralization may work sufficiently in ambient indoor air conditioned to 37 percent relative humidity and 23°C, but not in zero nitrogen. This latter environment may require that the permeation device sit for more time on the antistatic strip. The longer neutralization period may have to be done inside the weighing chamber or a second small chamber, which is used just for charge neutralization.

### 3.4.4 Weighing Interval

The minimum time period between weighings of the candidate standard is a function of the expected permeation rate, the specified uncertainty for the rate, and the analytical balance's readability (i.e., the smallest scale division). The following equation is based on a  $\pm 1$  percent uncertainty specification for the permeation rate:

where the weighing interval is in minutes; the readability is in grams; and the expected permeation rate

$$\text{Minimum Weighing Interval} = \frac{100 (\text{Readability})}{(\text{Expected Permeation Rate})}$$

is in grams per minute.

### 3.4.5 Assay Procedure

1. Turn on the balance and allow it to warm up for the period specified in the operator's manual. To ensure maximum stability, it is recommended to keep the balance turned on at all times. This procedure enables the balance to be operational at all times and eliminates the need for a warmup period before analyses. Newer balances are always turned on (except for their displays) when they are plugged in.
2. Check the balance level and, if necessary, adjust the level according to the manufacturer's instructions.
3. Ensure that the balance room temperature is within 15 to 30 °C or, if given, within the balance manufacturer's specifications and that the balance and mass reference standards are equilibrated to the balance room temperature. Record the temperature in the laboratory's records.
4. Zero (i.e., tare) and calibrate the balance according to the manufacturer's directions. Record the tare reading in the laboratory's records. Many newer balances calibrate themselves automatically or only require a key to be touched to calibrate themselves.
5. On each day that the candidate standard is to be assayed, verify the balance's calibration using at least two NIST-traceable mass reference standards. Use smooth, nonmetallic forceps to handle the standards. This standard must have a mass that is similar to that of the candidate standard. Record the date, balance identification, standards identification, certified weight of the standard, and the measured weight of the standard in the laboratory's records. Calculate the relative difference (in percent) between the certified and measured weights as follows:  
Record the relative difference in the laboratory's records. If the relative difference is

$$\text{Relative Difference} = \frac{100 (\text{Measured Weight} - \text{Certified Weight})}{(\text{Certified Weight})}$$

>0.1 percent, the balance cannot be used under this protocol until it has been recalibrated or repaired and until a subsequent verification has a relative difference of 0.1 percent.

6. Review the recorded bath or chamber temperature readings since the most recent weighing of the candidate standard, or since the standard was first put into the temperature-controlled chamber. Record the minimum and maximum temperatures in the laboratory's records. The minimum and maximum temperatures must not have deviated from the setpoint by more than 0.1 °C. If these temperatures deviate by more than this amount, the current assay and all previous assays are invalidated.
7. Record the current bath or chamber temperature in the laboratory's records.
8. Verify that the candidate standard has been in the temperature-controlled chamber for a long enough time for its permeation rate to have stabilized.
9. Remove the candidate standard from the temperature-controlled chamber and place it on the balance's pan using stainless steel forceps or a similar noncontaminating device. Note that Teflon<sup>®</sup> permeation tubes may have an electrostatic charge buildup due to the passage of the dry gas over them between weighings. Such charges should be removed from the candidate

standard before weighing by Po<sup>210</sup> antistatic strips or similar devices. Note that electronic force balances may require that candidate standards be thermally equilibrated before they can be weighed.

10. Record the date, time and the candidate standard's identification number and current weight in the laboratory's records.
11. Return the candidate standard to the temperature-controlled chamber. The standard should be outside the chamber only for a long enough time to weigh it using reasonable laboratory technique.

### 3.4.6 Number of Weighings of the Candidate Standard

The candidate standard must be weighed at least six times after its permeation rate has stabilized at the certification temperature. After the six or more weighings, the analyst may assess the stability and uncertainty of the permeation rate by using the spreadsheet described in Appendix B or equivalent statistical or graphic techniques. The analyst may calculate a provisional permeation rate from the measured weights and the time between weighings using the following equation:

$$\text{Provisional Permeation Rate} = \frac{(\text{Previous Weight} - \text{Current Weight})}{\text{Elapsed Time Between Weighings}}$$

Based on this data analysis, the analyst may perform additional weighings to reduce the uncertainty or to replace data that are discarded because they were obtained before the permeation rate stabilized.

### 3.4.7 Calculation of Certified Permeation Rate

The certified permeation rate for the candidate standard is the slope of the least squares regression line for data from at least six weighings of the candidate standard after the permeation rate has stabilized. This statistical analysis technique produces permeation rate estimates that are more precise than those calculated from weight differences between individual weighings. Although the minimum number of weighings is six, more precise estimates will be obtained for more weighings.

Calculate the certified permeation rate and its uncertainty using the spreadsheet given in Appendix B or using equivalent statistical techniques (e.g., the worksheet for linear relationships given in Chapter 5 of Reference 15). Figure 3-4 presents an example of the graphic output of the spreadsheet. This rate is the slope ( $b_1$ ) of the least squares regression line where the x-values are the elapsed times from the initial weighing and the y-values are the measured weights of the permeation device. The

spreadsheet also calculates the predicted initial weight ( $b_0$ ) of the permeation device and 95-percent confidence limits for  $b_0$  and  $b_1$ .

After the data from the six or more weighings have been entered in the spreadsheet, examine the 95-percent confidence limits (CLs) for  $b_0$ . If the measured weight from the initial weighing falls outside of these limits, the permeation device may not have been completely equilibrated at the initial weighing. The analyst may elect to discard the data from the initial weighing to reduce the uncertainty of the certified permeation rate.

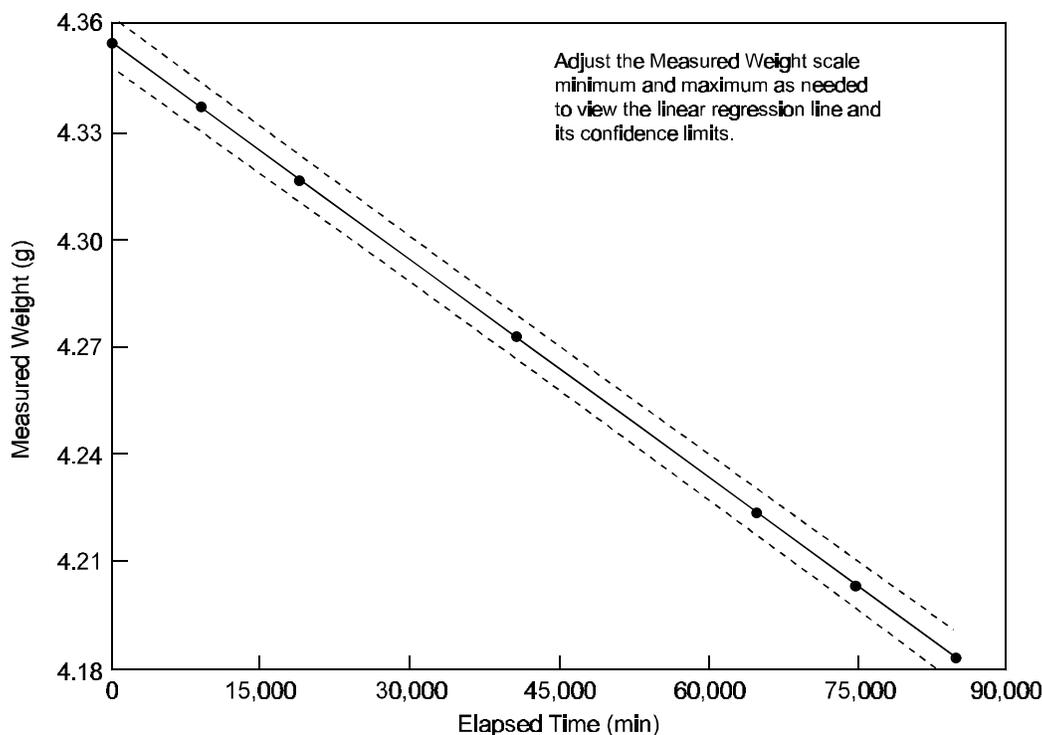
Examine the upper and lower 95-percent CLs for  $b_1$ . They should differ from  $b_1$  by no more than 1 percent of its value. That is,

If these two criteria are met, the permeation device can be certified with a permeation rate equal

$$\text{upper CL}(b_1) - b_1 \leq (b_1)/100 .$$

$$b_1 - \text{lower CL}(b_1) - b_1 \leq (b_1)/100 .$$

to  $b_1$  and an uncertainty equal to the larger of the two values. If the criteria are not met, the analyst must make additional weighings of the candidate standard as described in Subsection 3.4.5. These additional measurements will be pooled with the previously collected measurements. The pooled data will be used to obtain new estimates of the  $b_1$  and its uncertainty. When an acceptable value for the uncertainty is obtained, record it and the slope in the laboratory's records. If an acceptable value is not obtained, the candidate standard cannot be certified under this protocol.



**Figure 3-4. Example of spreadsheet graphic output for calculating permeation rates.**

The analyst should investigate any of the measurements that appear to be outliers. Such data may be discarded if the analyst can demonstrate that the experimental conditions were inappropriate during these measurements. Data cannot be discarded just because they appear to be outliers but may be discarded if they satisfy statistical criteria for testing outliers. The analyst must record any discarded data and a brief summary of the investigation in the laboratory's records.

### **3.4.8 Uncertainty of Certified Permeation Rate for Candidate Standard**

The total analytical uncertainty of the certified permeation rate includes the uncertainty of regression slope and the uncertainty of the mass reference standard that was used to verify the balance's calibration. The two components are combined using the following equation for the propagation of errors:

$$\frac{\text{Uncertainty (Total)}}{\text{Permeation Rate}} = \left[ \left( \frac{\text{Uncertainty (Slope)}}{\text{Slope}} \right)^2 + \left( \frac{\text{Uncertainty (Mass)}}{\text{Mass}} \right)^2 \right]^{1/2}$$

### **3.4.9 Certification Documentation**

See Subsections 3.1.5 and 3.1.6.

### **3.4.10 Recertification Requirements**

See Subsection 3.1.7.3.

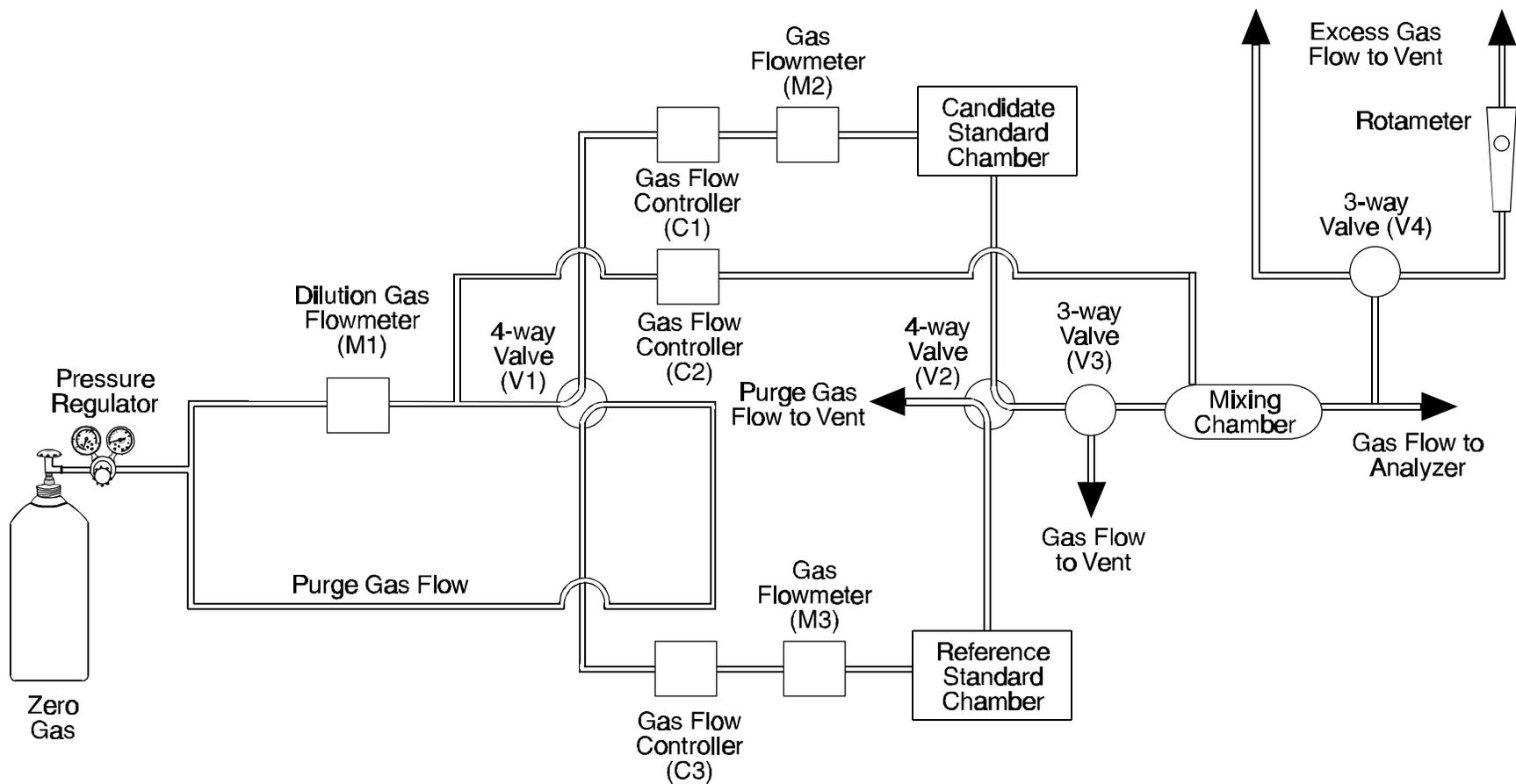


Figure 3-1. One possible design of the apparatus for the assay of permeation device calibration standards referenced to a permeation device reference standard (Procedure P1).

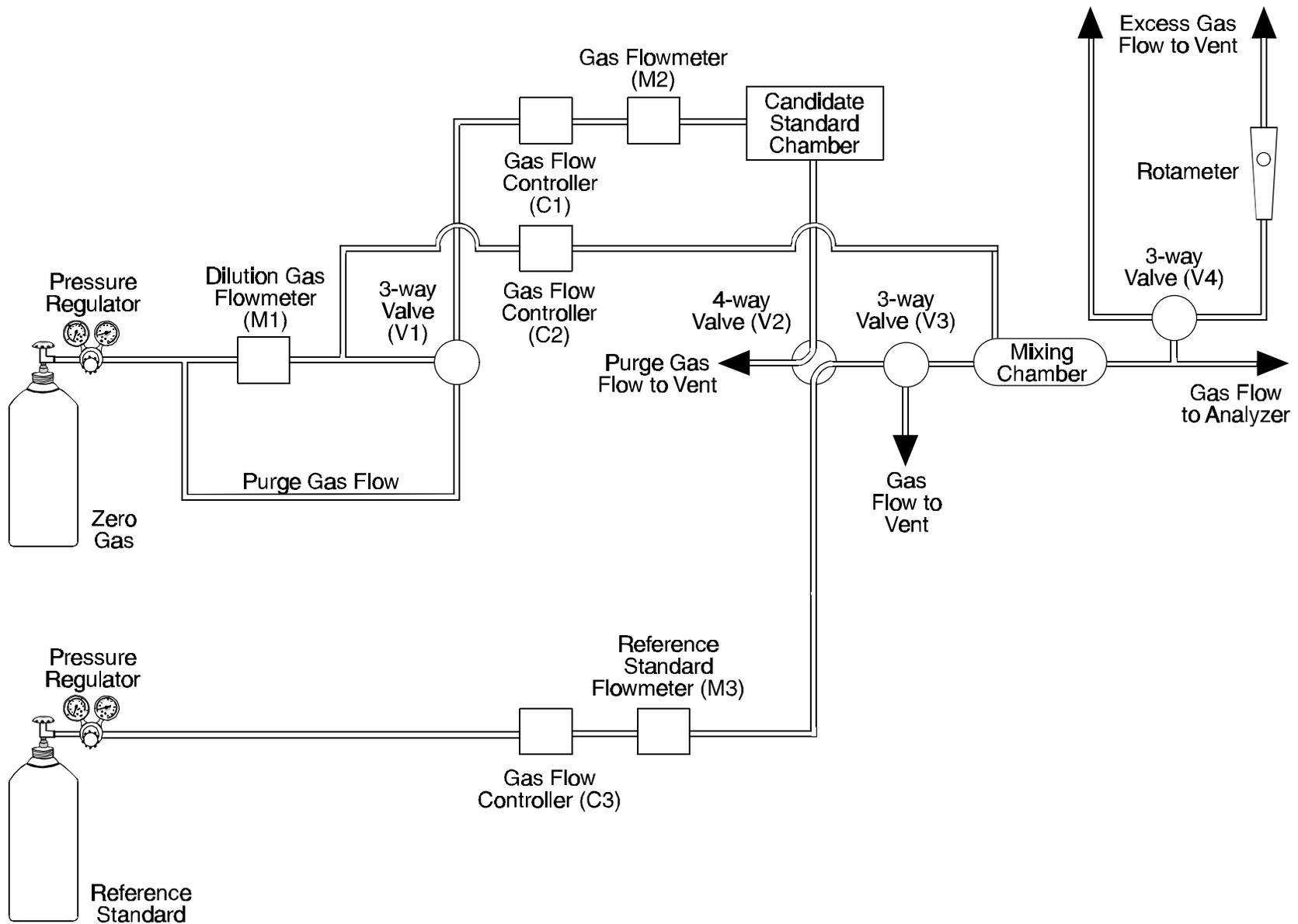


Figure 3-2. One possible design of the apparatus for the assay of permeation device calibration standards referenced to a compressed gas reference standard (Procedure P2).