APPENDIX A

SAMPLING AND ANALYTICAL PROCEDURES

METHOD 1—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. To aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source, a measurement site where the effluent stream is flowing in a known direction is selected, and the cross-section of the stack is divided into a number of equal areas. A traverse point is then located within each of these equal areas.

1.2 Applicability. This method is applicable to flowing gas streams in ducts, stacks, and flues. The method cannot be used when: (1) flow is cyclonic or swirling (see Section 2.4), (2) a stack is smaller than about 0.30 meter (12 in.) in diameter, or 0.071 m² (113 in.²) cross-sectional area, or (3) the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

The requirements of this method must be considered before construction of a new facility from which emissions will be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases involving variants are subject to approval by the Administrator, U.S. Environmental Protection Agency.

2. *Procedure*

2.1 Selection of Measurement Site. Sampling or velocity measurement is performed at a site located at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack, or from a visible flame. If necessary, an alternative location may be selected, at a position at least two stack or duct diameters downstream and a half diameter upstream from any flow disturbance. For a rectangular cross section, an equivalent diameter (D_e) shall be calculated from the following equation, to determine the upstream and downstream distances:

$$D_e = \frac{2\,LW}{(L+W)}$$

where L=length and W=width.

An alternative procedure is available for determining the acceptability of a measurement location not meeting the criteria above. This precedure, determination of gas flow angles at the sampling points and comparing the results with acceptability criteria, is described in Section 2.5.

2.2 Determining the Number of Traverse Points.

2.2.1 Particulate Traverses. When the eight- and two-diameter criterion can be met, the minimum number of traverse points shall be: (1) twelve, for circular or rectangular stacks with diameters (or equivalent diameters) greater than 0.61 meter (24 in.); (2) eight, for circular stacks with diameters between 0.30 and 0.61 meter (12-24 in.); (3) nine, for rectangular stacks with equivalent diameters between 0.30 and 0.61 meter (12-24 in.).

When the eight- and two-diameter criterion cannot be met, the minimum number of traverse points is determined from Figure 1-1. Before referring to the figure, however, determine the distances from the chosen measurement site to the nearest upstream and downstream disturbances, and divide each distance by the stack diameter or equivalent diameter, to determine the distance in terms of the number of duct diameters. Then, determine from Figure 1-1 the minimum number of traverse points that corresponds: (1) to the number of duct diameters upstream; and (2) to the number of diameters downstream. Select the higher of the two minimum numbers of traverse points, or a greater value, so that for circular stacks the number is a multiple of 4, and for rectangular stacks, the number is one of those shown in Table 1-1.

TABLE 1-1. CROSS-SECTION LAYOUT FOR RECTANGULAR STACKS

Number of traverse points	Matrix layout
9	3x3
12	4x3
16	4x4
20	5x4
25	5x5
30	6x5
36	6x6
42	7x6
49	7x7

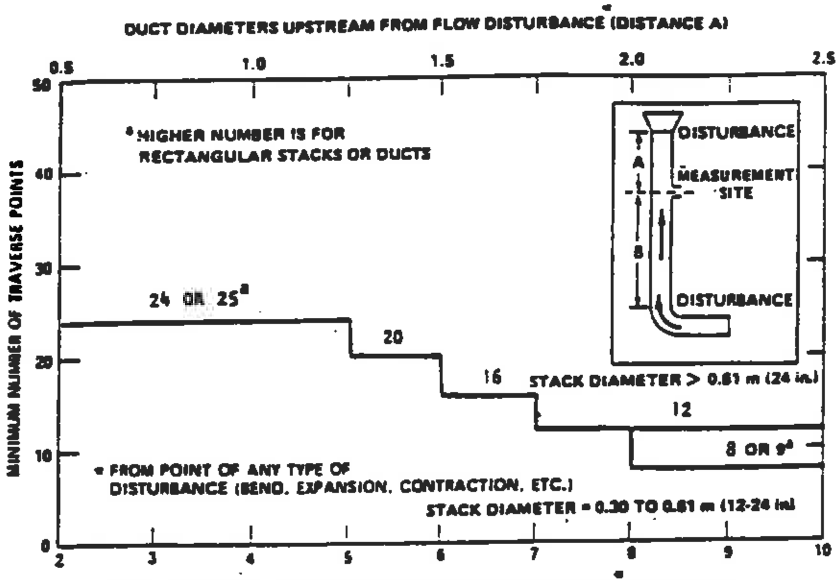

Figure 1-1. Minimum number of traverse points for particulate traverses.

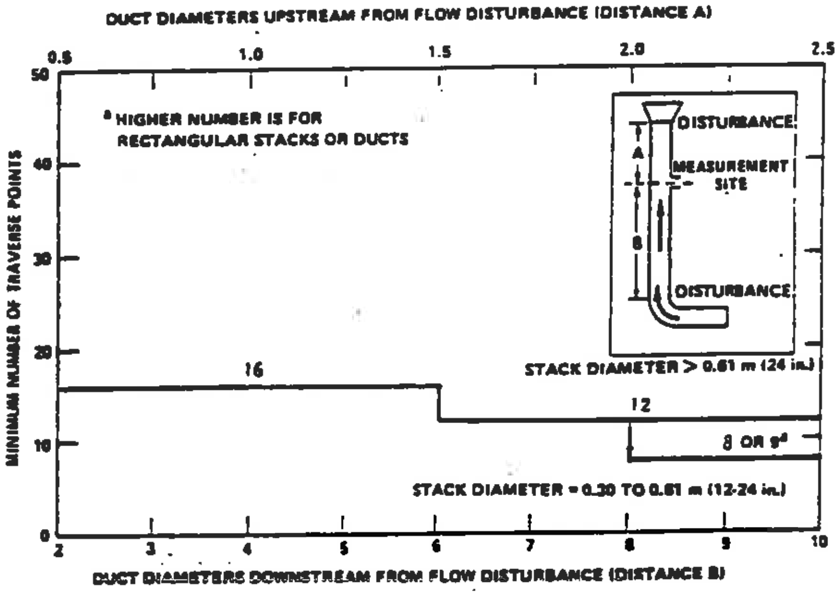

Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

2.2.2 Velocity (Non-Particulate) Traverses. When velocity or volumetric flow rate is to be determined (but not particulate matter), the same procedure as that for particulate traverses (Section 2.2.1) is followed, except that Figure 1-2 may be used instead of Figure 1-1.

2.3 Cross-sectional Layout and Location of Traverse Points.

2.3.1 Circular Stacks. Locate the traverse points on two perpendicular diameters according to Table 1-2 and the example shown in Figure 1-3. Any equation (for examples, see Citations 2 and 3 in the Bibliography) that gives the same values as those in Table 1-2 may be used in lieu of Table 1-2.

For particulate traverses, one of the diameters must be in a plane containing the greatest expected concentration variation, e.g., after bends, one diameter shall be in the plane of the bend. This requirement becomes less critical as the distance from the disturbance increases: therefore, other diameter locations may be used, subject to approval of the Administrator.

In addition for stacks having diameters greater than 0.61 m (24 in.) no traverse points shall be located within 2.5 centimeters (1.00 in.) of the stack walls: and for stack diameters equal to or less than 0.61 m (24 in.), no traverse points shall be located within 1.3 cm (0.50 in.) of the stack walls. To meet these criteria, observe the procedures given below.

2.3.1.1 Stacks With Diameters Greater Than 0.61 m (24 in.). When any of the traverse points as located in Section 2.3.1 fall within 2.5 cm (1.00 in.) of the stack walls, relocate them away from the stack walls to: (1) a distance of 2.5 cm (1.00 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger. These relocated traverse points (on each end of a diameter) shall be the "adjusted" traverse points.

Whenever two successive traverse points are combined to form a single adjusted traverse point, treat the adjusted point as two separate traverse points, both in the sampling (or velocity measurement) procedure, and in recording the data.

TRAVERSE POINT	DISTANCE, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6

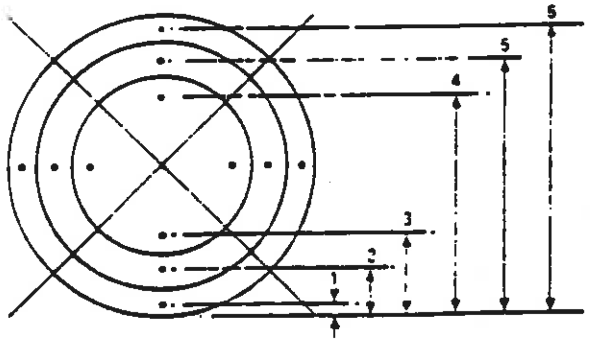

Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

TABLE 1-2. LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS

(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter—											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

2.3.1.2 Stacks With Diameters Equal to or Less Than 0.61 m (24 in.). Follow the procedure in Section 2.3.1.1, noting only that any "adjusted" points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

2.3.2 Rectangular Stacks. Determine the number of traverse points as explained in Sections 2.1 and 2.2 of this method. From Table 1-1, determine the grid configuration. Divide the stack cross-section into as many equal rectangular elemental areas as traverse points, and then locate a traverse point at the centroid of each equal area according to the example in Figure 1-4.

If the tester desires to use more than the minimum number of traverse points, expand the "minimum number of traverse points" matrix (see Table 1-1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4x3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9x4 or 12x3, and would not necessarily have to be 6x6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

The situation of traverse points being too close to the stack walls is not expected to arise with rectangular stacks. If this problem should ever arise, the Administrator must be contacted for resolution of the matter.

2.4 Verification of Absence of Cyclonic Flow. In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

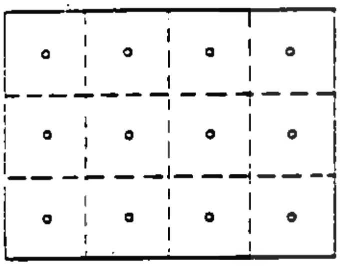

Figure 1-4. Example showing rectangular stack cross section divided into 12 equal areas, with a traverse point at centroid of each area.

Level and zero the manometer. Connect a Type S pitot tube to the manometer. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane: when the Type S pitot tube is in this position, it is at "0° reference." Note the differential pressure (Δp) reading at each traverse point. If a null (zero) pitot reading is obtained at 0° reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0° reference, rotate the pitot tube (up to ±90° yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (α) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of α; assign α values of 0° to those points for which no rotation was required, and include these in the overall average. If the average value of α is greater than 20°, the overall flow condition in the stack is unacceptable and alternative methodology, subject to the approval of the Administrator, must be used to perform accurate sample and velocity traverses.

The alternative procedure described in Section 2.5 may be used to determine the rotation angles in lieu of the procedure described above. The limit of acceptability for the average value of α would remain 20°.

2.5 Alternative Measurement Site Selection Procedure. This alternative applies to sources where measurement locations are less than 2 equivalent stack or duct diameters downstream or less than ½ duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 in. in diameter where blockage and wall effects are minimal. A directional flow-sensing probe is used to measure pitch and yaw angles of the gas flow at 40 or more traverse points; the resultant angle is calculated and compared with acceptable criteria for mean and standard deviation.

Note.—Both the pitch and yaw angles are measured from a line passing through the traverse point and parallel to the stack axis. The pitch angle is the angle of the gas flow component in the plane that INCLUDES the traverse line and is parallel to the stack axis. The yaw angle is the angle of the gas flow component in the plane PERPENDICULAR to the traverse line at the traverse point and is measured from the line passing through the traverse point and parallel to the stack axis.

2.5.1 Apparatus.

2.5.1.1 Directional Probe. Any directional probe, such as United Sensor Type DA Three-Dimensional Directional Probe, capable of measuring both the pitch and yaw angles of gas flows is acceptable. (Note: Mention of trade name or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Assign an identification number to the directional probe, and permanently mark or engrave the number on the body of the probe. The pressure holes of directional probes are susceptible to plugging when used in particulate-laden gas streams. Therefore, a system for cleaning the pressure holes by "back-purging" with pressurized air is required.

2.5.1.2 Differential Pressure Gauges. Inclined manometers, U-tube manometers, or other differential pressure gauges (e.g., magnehelic gauges) that meet the specifications described in Method 2, § 2.2.

Note.—If the differential pressure gauge produces both negative and positive readings, then both negative and positive pressure readings shall be calibrated at a minimum of three points as specified in Method 2, § 2.2.

2.5.2 Traverse Points. Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations. Follow § 2.3 and Table 1-1 or 1-2 for the location and layout of the traverse points. If the measurement location is determined to be acceptable according to the criteria in this alternative procedure, use the same traverse point number and locations for sampling and velocity measurements.

2.5.3 Measurement Procedure.

2.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer. Capillary tubing or surge tanks may be used to dampen pressure fluctuations. It is recommended, but not required, that a pretest leak check be conducted. To perform a leak check, pressurize or use suction on the impact opening until a reading of at least 7.6 cm (3 in.) H_2O registers on the differential pressure gauge, then plug the impact opening. The pressure of a leak-free system will remain stable for at least 15 seconds.

2.5.3.2 Level and zero the manometers. Since the manometer level and zero may drift because of vibrations and temperature changes, periodically check the level and zero during the traverse.

2.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point. Complete a "back-purge" of the pressure lines and the impact openings prior to measurements of each traverse point.

A post-test check as described in § 2.5.3.1 is required. If the criteria for a leak-free system are not met, repair the equipment, and repeat the flow angle measurements.

2.5.4 Calculate the resultant angle at each traverse point, the average resultant angle, and the standard deviation using the following equations. Complete the calculations retaining at least one extra significant figure beyond that of the acquired data. Round the values after the final calculations.

2.5.4.1 Calculate the resultant angle at each traverse point:

$R_i = \text{arc cosine}\,[(\text{cosine } Y_i)(\text{cosine } P_i)]$ Eq. 1-2

Where:

R = Resultant angle at traverse point i. degree.

Y_i = Yaw angle at traverse point i. degree.

P_i = Pitch angle at traverse point i. degree.

2.5.4.2 Calculate the average resultant for the measurements:

$$\bar{R} = \frac{\Sigma R_i}{n} \qquad \text{Eq. 1-3}$$

where:

$\bar{R}$ = Average resultant angle. degree.

n = Total number of traverse points.

2.5.4.3 Calculate the standard deviations:

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{(n-1)}} \qquad \text{Eq. 1-4}$$

Where:

S_d = Standard deviation. degree.

2.5.5 The measurement location is acceptable if $\bar{R} < 20°$ and $S_d < 10°$.

2.5.6 Calibration. Use a flow system as described in Sections 4.1.2.1 and 4.1.2.2 of Method 2. In addition, the flow system shall have the capacity to generate two test-section velocities: one between 365 and 730 m/min (1200 and 2400 ft/min) and one between 730 and 1100 m/min (2400 and 3600 [illegible]

2.5.6.1 Cut two entry ports in the test section. The axes through the entry ports shall be perpendicular to each other and intersect in the centroid of the test section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should be constructed of plexiglass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test-section.

2.5.6.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure in Section 2.4 for cyclonic flow determination to measure the gas flow angles at the centroid of the test section from two test ports located 90° apart. The gas flow angle measured in each port must be ± 2° of 0°. Straightening vanes should be installed, if necessary, to meet this criterion.

2.5.6.3 Pitch Angle Calibration. Perform a calibration traverse according to the manufacturer's recommended protocol in 5° increments for angles from −60° to +60° at one velocity in each of the two ranges specified above. Average the pressure ratio values obtained for each angle in the two flow ranges, and plot a calibration curve with the average values of the pressure ratio (or other suitable measurement factor as recommended by the manufacturer) versus the pitch angle. Draw a smooth line through the data points. Plot also the data values for each traverse point. Determine the differences between the measured data values and the angle from the calibration curve at the same pressure ratio. The difference at each comparison must be within 2° for angles between 0° and 40° and within 3° for angles between 40° and 60°.

2.5.6.4 Yaw Angle Calibration. Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening. To determine the accuracy of measurements of the yaw angle, only the zero or null position need be calibrated as follows. Place the directional probe in the test section, and rotate the probe until the zero position is found. With a protractor or other angle measuring device, measure the angle indicated by the yaw angle indicator on the three-demensional probe. This should be within 2° of 0°. Repeat this measurement for any other points along the length of the pitot where yaw angle measurements could be read in order to account for variations in the pitot markings used to indicate pitot head positions.

3. *Bibliography*

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METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

1. *Principle and Applicability*

1.1 Principle. The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube.

1.2 Applicability. This method is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow.

This procedure is not applicable at measurement sites which fail to meet the criteria of Method 1, Section 2.1. Also, the method cannot be used for direct measurement in cyclonic or swirling gas streams; Section 2.4 of Method 1 shows how to determine cyclonic or swirling flow conditions. When unacceptable conditions exist, alternative procedures, subject to the approval of the Administrator, U.S. Environmental Protection Agency, must be employed to make accurate flow rate determinations; examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically, or (3) to move to another measurement site at which the flow is acceptable.

2. *Apparatus*

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

2.1 Type S Pitot Tube. The Type S pitot tube (Figure 2-1) shall be made of metal tubing (e.g. stainless steel). It is recommended that the external tubing diameter (dimension D_t Figure 2-2b) be between 0.48 and 0.95 centimeters (3/16 and 3/8 inch). There shall be an equal distance from the base of each leg of the pitot tube to its face-opening plane (dimensions P_A and P_B Figure 2-2b); it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned as shown in Figure 2-2; however, slight misalignments of the openings are permissible (see Figure 2-3).

The Type S pitot tube shall have a known coefficient, determined as outlined in Section 4. an identification number shall be assigned to the pitot tube; this number shall be permanently marked or engraved on the body of the tube.

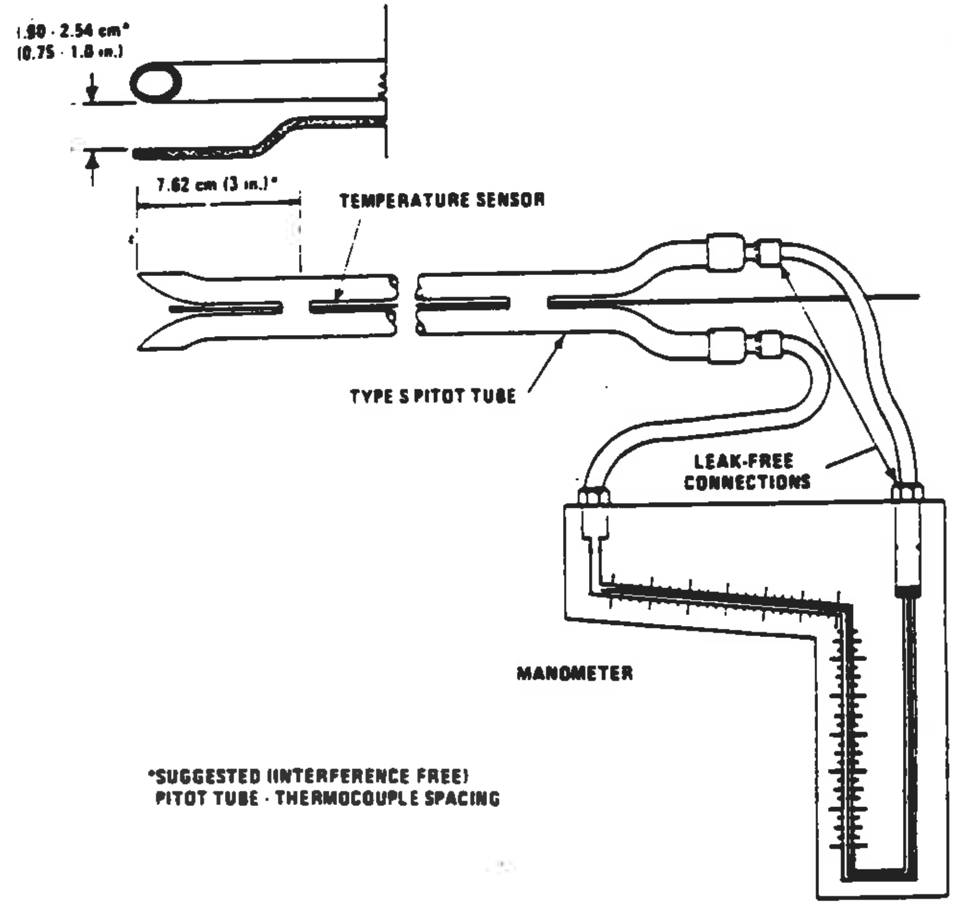


Figure 2-1. Type S pitot tube manometer assembly.

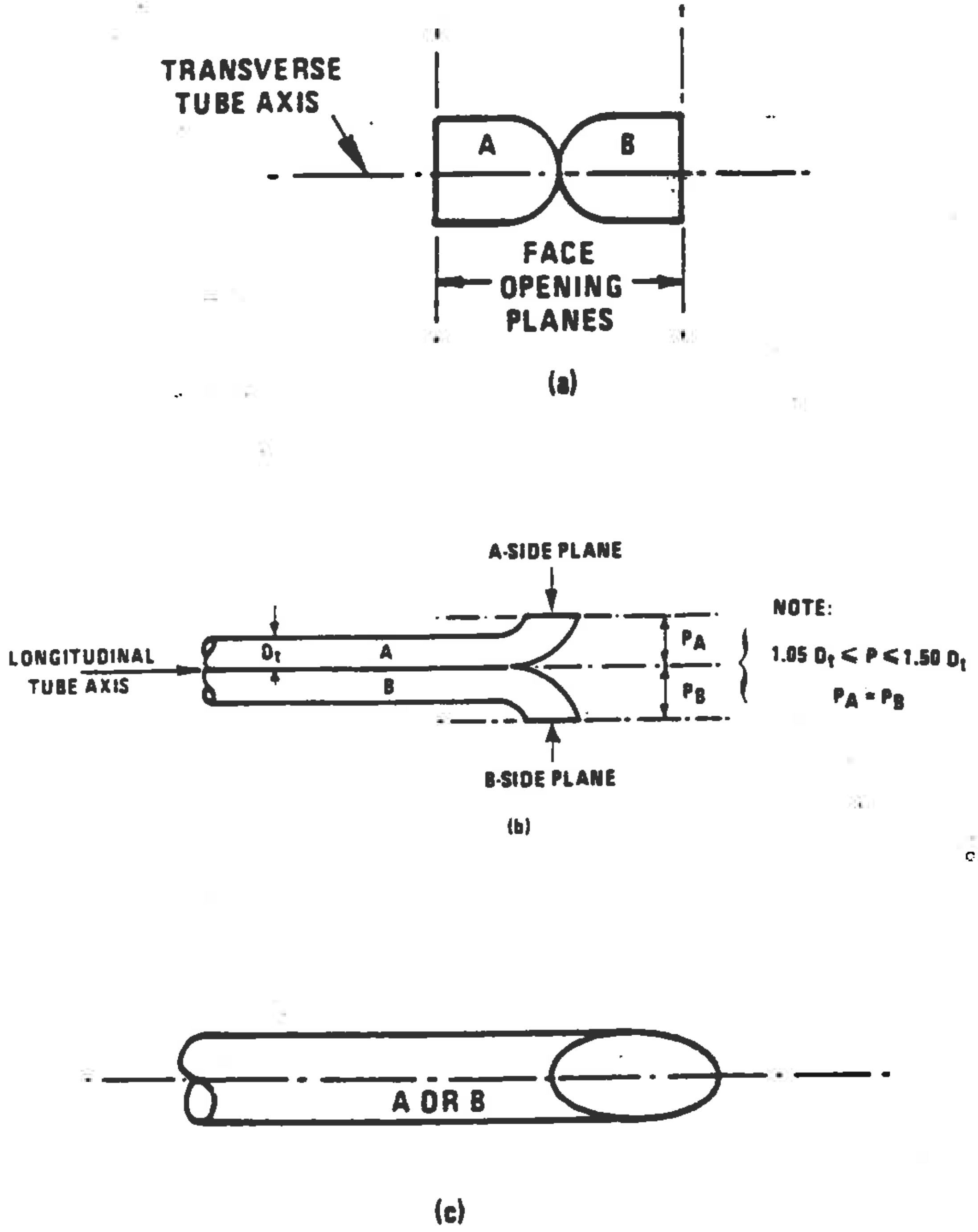


Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

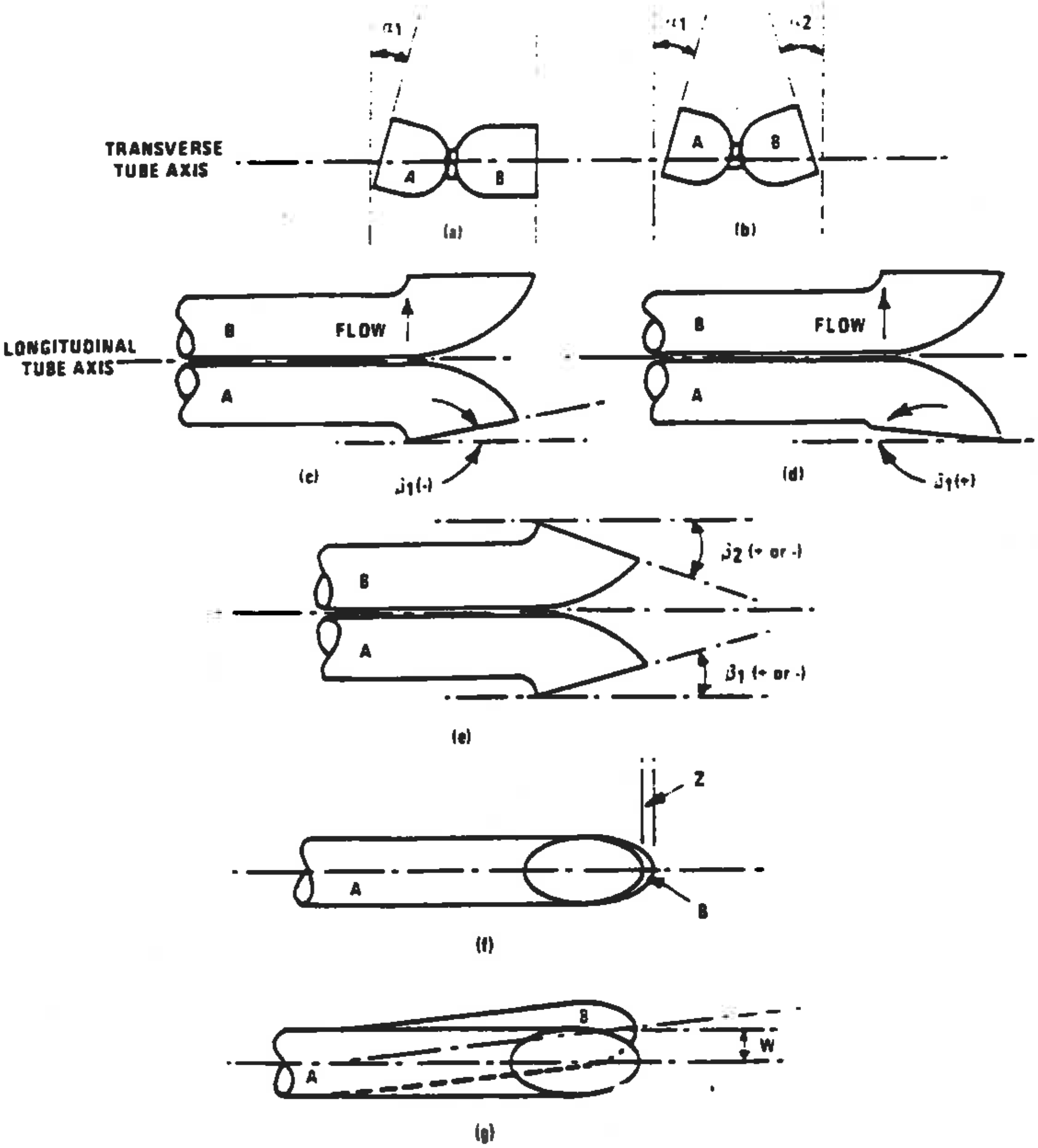


Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of Cp(s) so long as α1 and α2 10°, β1 and β2 5°, z 0.32 cm (1/8 in.) and w 0.08 cm (1/32 in.) (citation 11 in Section 6).

A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of Sections 2.7 and 4.2; note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (Δp) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another Δp reading. If the Δp readings made before and after the air purge are the same (±5 percent), the traverse is acceptable. Otherwise, reject the run. Note that if Δp at the final traverse point is unsuitably low, another point may be selected. If "back-purging" at regular intervals is part of the procedure, then comparative Δp readings shall be taken, as above, for the last two back purges at which suitably high Δp readings are observed.

2.2 Differential Pressure Gauge. An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10-in. (water column) inclined-vertical manometer, having 0.01-in. H_2O divisions on the 0-to 1-in. inclined scale, and 0.1-in. H_2O divisions on the 1- to 10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H_2O. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than 1.3 mm (0.05 in.) H_2O; (2) for traverses of 12 or more points, more than 10 percent of the individual Δp readings are below 1.3 mm (0.05 in.) H_2O; (3) for traverses of fewer than 12 points, more than one Δp reading is below 1.3 mm (0.05 in.) H_2O. Citation 18 in Section 6 describes commercially available instrumentation for the measurement of low-range gas velocities.

As an alternative to criteria (1) through (3) above, the following calculation may be performed to determine the necessity of using a more sensitive differential pressure gauge:

$$T=\frac{\sum_{i=1}^{n}\sqrt{\Delta p_i+K}}{\sum_{i=1}^{n}\sqrt{\Delta p_i}}$$

where:

Δp_i=Individual velocity head reading at a traverse point, mm H_2O (in. H_2O).

n=Total number of traverse points.

K=0.13 mm H_2O when metric units are used and 0.005 in H_2O when English units are used.

If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

NOTE: If differential pressure gauges other than inclined manometers are used (e.g., magnehelic gauges), their calibration must be checked after each test series. To check the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of Δp values in the stack. If, at each point, the values of Δp as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured Δp values and final results shall be used subject to the approval of the Administrator.

2.3 Temperature Gauge. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge, capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature shall be used. The temperature gauge shall be attached to the pitot tube such that the sensor tip does not touch any metal; the gauge shall be in an interference-free arrangement with respect to the pitot tube face openings (see Figure 2-1 and also Figure 2-7 in Section 4). Alternate positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of Section 4. Provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the temperature gauge need not be attached to the pitot tube; this alternative is subject to the approval of the Administrator.

2.4 Pressure Probe and Gauge. A piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg is used. The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face opening planes positioned parallel to the gas flow may also be used as the pressure probe.

2.5 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm (0.1 in.) Hg per 30-meter (100 foot) elevation increase or vice-versa for elevation decrease.

2.6 Gas Density Determination Equipment. Method 3 equipment, if needed (see Section 3.6), to determine the stack gas dry molecular weight, and Reference Method 4 or Method 5 equipment for moisture content determination; other methods may be used subject to approval of the Administrator.

2.7 Calibration Pitot Tube. When calibration of the Type S pitot tube is necessary (see Section 4), a standard pitot tube is used as a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Bureau of Standards, Route 270, Quince Orchard Road, Gaithersburg, Maryland, or (2) by calibration against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in 2.7.1 through 2.7.5 below and illustrated in Figure 2-4 (see also Citations 7, 8, and 17 in Section 6) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99±0.01.

2.7.1 Hemispherical (shown in Figure 2-4), ellipsoidal, or conical tip.

2.7.2 A minimum of six diameters straight run (based upon D, the external diameter of the tube) between the tip and the static pressure holes.

2.7.3 A minimum of eight diameters straight run between the static pressure holes and the centerline of the external tube, following the 90 degree bend.

2.7.4 Static pressure holes of equal siz (approximately 0.1 D), equally spaced in a piezometer ring configuration.

2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type S Pitot Tube Calibration. An inclined manometer or equivalent is used. If the single-velocity calibration technique is employed (see Section 4.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.13 mm H_2O (0.005 in. H_2O). For multivelocity calibrations, the gauge shall be readable to the nearest 0.13 mm H_2O (0.005 in H_2O) for Δp values between 1.3 and 25 mm H_2O (0.05 and 1.0 in. H_2O), and to the nearest 1.3 mm H_2O (0.05 in. H_2O) for Δp values above 25 mm H_2O (1.0 in. H_2O). A special, more sensitive gauge will be required to read Δp values below 1.3 mm H_2O [0.05 in. H_2O] (see Citation 18 in Section 6).

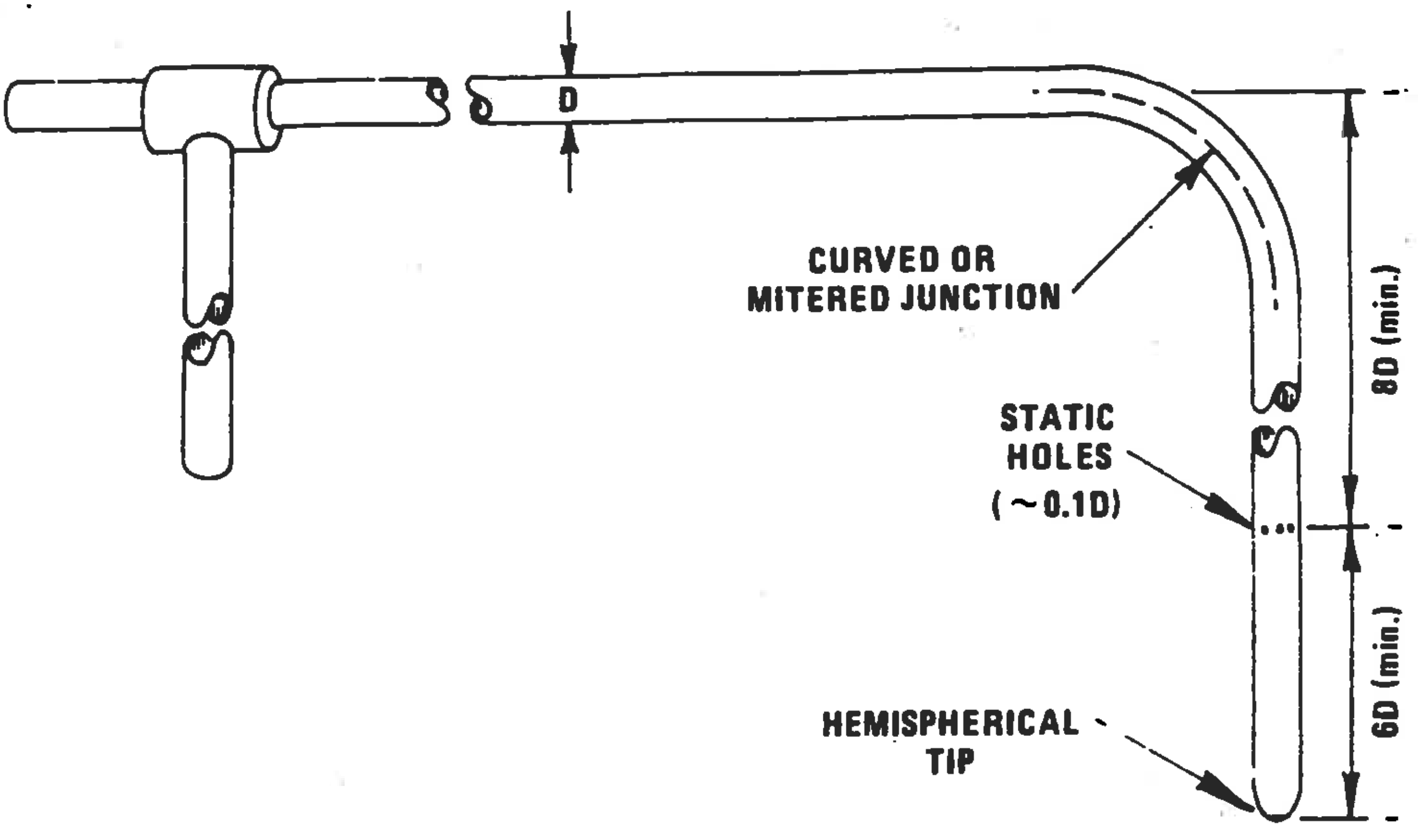


Figure 2-4. Standard pitot tube design specifications.

3. *Procedure*

3.1 Set up the apparatus as shown in Figure 2-1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen Δp fluctuations. It is recommended, but not required, that a pretest leak-check be conducted, as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3 in.) H_2O velocity pressure registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3 in.) H_2O. Other leak-check procedures, subject to the approval of the Administrator may be used.

3.2 Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse. Record all necessary data as shown in the example data sheet (Figure 2-5).

3.3 Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of Δp values encountered (see Section 2.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the Δp and temperature readings at each traverse point. Conduct a post-test leak-check (mandatory), as described in Section 3.1 above, to validate the traverse run.

3.4 Measure the static pressure in the stack. One reading is usually adequate.

3.5 Determine the atmospheric pressure.

PLANT ____________________
DATE __________ RUN NO. __________
STACK DIAMETER OR DIMENSIONS, m(in.) __________
BAROMETRIC PRESSURE, mm Hg (in. Hg) __________
CROSS SECTIONAL AREA, $m^2(ft^2)$ __________
OPERATORS __________
PITOT TUBE I.D. NO. __________
AVG. COEFFICIENT, C_p = __________
LAST DATE CALIBRATED __________

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack Temperature		P_g mm Hg (in.Hg)	$\sqrt{\Delta p}$
		t_s, °C (°F)	T_s, °K (°R)		
		Average			

Figure 2-5. Velocity traverse data.

3.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO_2, O_2, CO, and N_2, use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other methods, subject to the approval of the Administrator, must be used.

3.7 Obtain the moisture content from Reference Method 4 (or equivalent) or from Method 5.

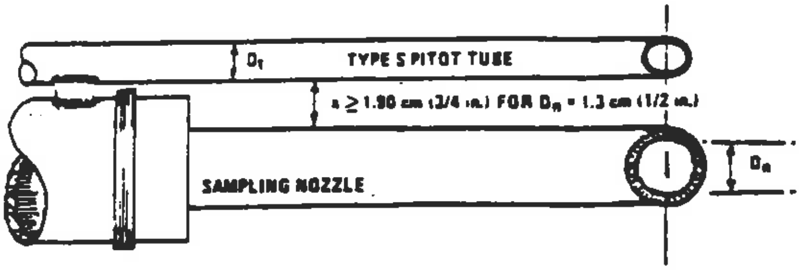
3.8 Determine the cross-sectional area of the stack or duct at the sampling location. Whenever possible, physically measure the stack dimensions rather than using blueprints.

4. *Calibration*

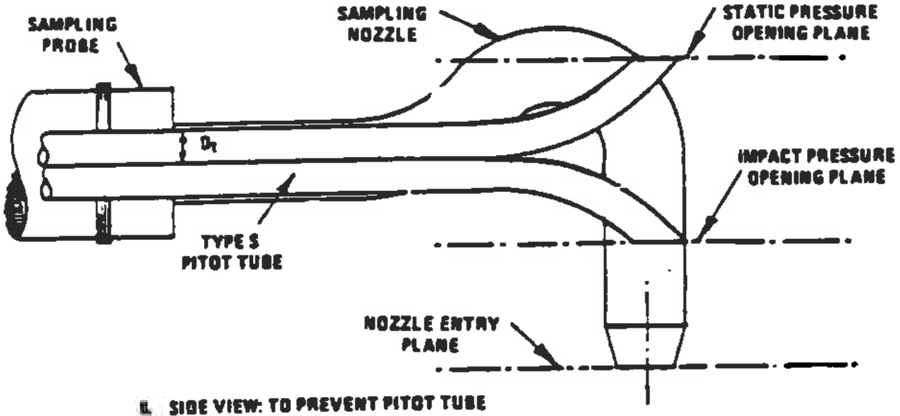
4.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube in top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figure 2-2 or 2-3. The pitot tube shall not be used if it fails to meet these alignment specifications.

After verifying the face opening alignment, measure and record the following dimensions of the pitot tube: (a) the external tubing diameter (dimension D_t, Figure 2-2b); and (b) the base-to-opening plane distances (dimensions P_A and P_B, Figure 2-2b). If D_t is between 0.48 and 0.95 cm (3/16 and 3/8 in.) and if P_A and P_B are equal and between 1.05 and 1.50 D_t, there are two possible options: (1) the pitot tube may be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, or (2) a baseline (isolated tube) coefficient value of 0.84 may be assigned to the pitot tube. Note, however, that if the pitot tube is part of an assembly, calibration may still be required, despite knowledge of the baseline coefficient value (see Section 4.1.1).

If D_t, P_A, and P_B are outside the speci
limits, the pitot tube must be calibrat
outlined in 4.1.2 through 4.1.5 below.



A. BOTTOM VIEW: SHOWING MINIMUM PITOT-NOZZLE SEPARATION.



B. SIDE VIEW: TO PREVENT PITOT TUBE FROM INTERFERING WITH GAS FLOW STREAMLINES APPROACHING THE NOZZLE. THE IMPACT PRESSURE OPENING PLANE OF THE PITOT TUBE SHALL BE EVEN WITH OR ABOVE THE NOZZLE ENTRY PLANE.

Figure 2-6. Proper pitot tube-sampling nozzle configuration to prevent aerodynamic interference; buttonhook-type nozzle; centers of nozzle and pitot opening aligned; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Citation 9 in Section 6); therefore an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2-6 through 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-6 through 2-8 shall be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, and prior to calibration, the values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

NOTE: Do not use any Type S pitot tube assembly which is constructed such that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle (see Figure 2-6b).

4.1.2 Calibration Setup. If the Type S pitot tube is to be calibrated, one leg of the tube shall be permanently marked A, and the other, B. Calibration shall be done in a flow system having the following essential design features:

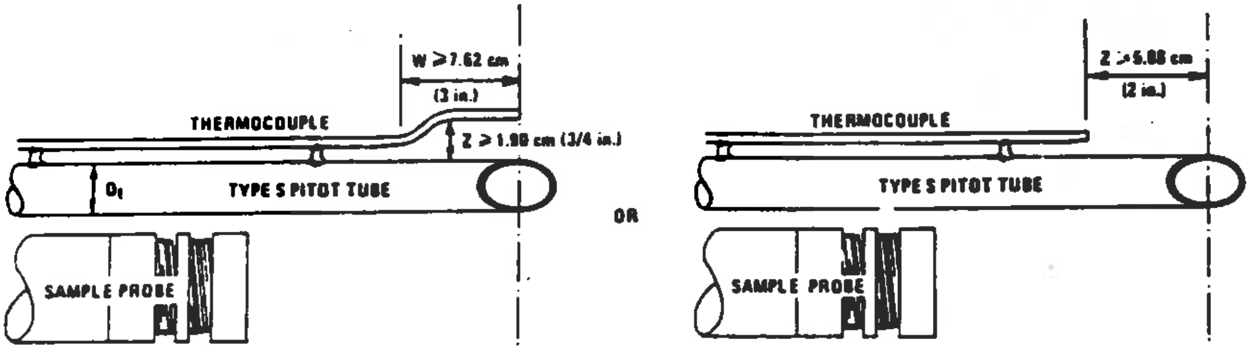


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

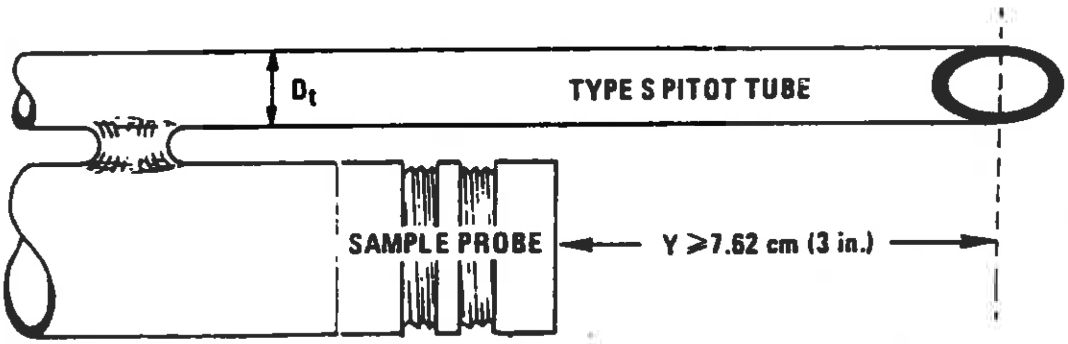


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.2.1 The flowing gas stream must be confined to a duct of definite cross-sectional area, either circular or rectangular. For circular cross-sections, the minimum duct diameter shall be 30.5 cm (12 in.); for rectangular cross-sections, the width (shorter side) shall be at least 25.4 cm (10 in.).

4.1.2.2 The cross-sectional area of the calibration duct must be constant over a distance of 10 or more duct diameters. For a rectangular cross-section, use an equivalent diameter, calculated from the following equation, to determine the number of duct diameters:

$$D = \frac{2LW}{(L+W)}$$

Equation 2-1

where:
D_e = Equivalent diameter
L = Length
W = Width

To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least eight diameters downstream and two diameters upstream from the nearest disturbances.

NOTE: The eight- and two-diameter criteria are not absolute; other test section locations may be used (subject to approval of the Administrator), provided that the flow at the test site is stable and demonstrably parallel to the duct axis.

4.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 915 m/min (3,000 ft/min). This velocity must be constant with time to guarantee steady flow during calibration. Note that Type S pitot tube coefficients obtained by single-velocity calibration at 915 m/min (3,000 ft/min) will generally be valid to within ±3 percent for the measurement of velocities above 305 m/min (1,000 ft/min) and to within ±5 to 6 percent for the measurement of velocities between 180 and 305 m/min (600 and 1,000 ft/min). If a more precise correlation between C_p and velocity is desired, the flow system shall have the capacity to generate at least four distinct, time-invariant test-section velocities covering the velocity range from 180 to 1,525 m/min (600 to 5,000 ft/min), and calibration data shall be taken at regular velocity intervals over this range (see Citations 9 and 14 in Section 6 for details).

4.1.2.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of plexiglas or some other transparent material.

4.1.3 Calibration Procedure. Note that this procedure is a general one and must not be used without first referring to the special considerations presented in Section 4.1.5. Note also that this procedure applies only to single-velocity calibration. To obtain calibration data for the A and B sides of the Type S pitot tube, proceed as follows:

4.1.3.1 Make sure that the manometer is properly filled and that the oil is free from contamination and is of the proper density. Inspect and leak-check all pitot lines; repair or replace if necessary.

PITOT TUBE IDENTIFICATION NUMBER: ________________ DATE: ____________

CALIBRATED BY: ______________________________

	"A" SIDE CALIBRATION			
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(s)}$	DEVIATION $C_{p(s)} - \bar{C}_p(A)$
1				
2				
3				
		$\bar{C}_p$ (SIDE A)		

	"B" SIDE CALIBRATION			
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(s)}$	DEVIATION $C_{p(s)} - \bar{C}_p(B)$
1				
2				
3				
		$\bar{C}_p$ (SIDE B)		

$$\text{AVERAGE DEVIATION} = \sigma\,(\text{A OR B}) = \frac{\sum_{1}^{3} \left| C_p(s) - \bar{C}_p(\text{A OR B}) \right|}{3} \longleftarrow \text{MUST BE} \leq 0.01$$

$$\left| \bar{C}_p\,(\text{SIDE A}) - \bar{C}_p\,(\text{SIDE B}) \right| \longleftarrow \text{MUST BE} \leq 0.01$$

Figure 2-9. Pitot tube calibration data.

4.1.3.2 Level and zero the manometer. Turn on the fan and allow the flow to stabilize. Seal the Type S entry port.

4.1.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in Section 4.1.5.1), and align the tube so that its tip is pointed directly into the flow. Particular car should be taken in aligning the tube to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.4 Read Δp_{std} and record its value in a data table similar to the one shown in Figure 2-9. Remove the standard pitot tube from the duct and disconnect it from the manometer. Seal the standard entry port.

4.1.3.5 Connect the Type S pitot tube to the manometer. Open the Type S entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its A side impact opening is at the same point as was the standard pitot tube and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.6 Read Δp_s and enter its value in the data table. Remove the Type S pitot tube from the duct and disconnect it from the manometer.

4.1.3.7 Repeat steps 4.1.3.3 through 4.1.3.6 above until three pairs of Δp readings have been obtained.

4.1.3.8 Repeat steps 4.1.3.3 through 4.1.3.7 above for the B side of the Type S pitot tube.

4.1.3.9 Perform calculations, as described in Section 4.1.4 below.

4.1.4 Calculations.

4.1.4.1 For each of the six pairs of Δp readings (i.e., three from side A and three from side B) obtained in Section 4.1.3 above calculate the value of the Type S pitot tu coeffficient as follows:

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_s}}$$

Equation 2-2

where:

$C_{p(s)}$ = Type S pitot tube coefficient

$C_{p(std)}$ = Standard pitot tube coefficient: use 0.99 if the coefficient is unknown and the tube is designed according to the criteria of Sections 2.7.1 to 2.7.5 of this method.

Δp_{std} = Velocity head measured by the standard pitot tube, cm H_2O (in. H_2O)

Δp_s = Velocity head measured by the Type S pitot tube, cm H_2O (in H_2O)

4.1.4.2 Calculate $\bar{C}_p$ (side A), the mean A-side coefficient, and $\bar{C}_p$ (side B), the mean B-side coefficient; calculate the difference between these two average values.

4.1.4.3 Calculate the deviation of each of the three A-side values of $\bar{C}_{p(s)}$ from $\bar{C}_p$ (side A), and the deviation of each B-side value of $\bar{C}_{p(s)}$ from $\bar{C}_p$ $\bar{C}_p$ (side B). Use the following equation:

$$\text{Deviation} = C_{p(s)} - \bar{C}_p(\text{A or B})$$

Equation 2-3

4.1.4.4 Calculate σ, the average deviation from the mean, for both the A and B sides of the pitot tube. Use the following equation:

$$\sigma\,(\text{side A or B}) = \frac{\sum_{1}^{3} |C_{p(s)} - \bar{C}_p(A \text{ or } B)|}{3}$$

Equation 2-4

4.1.4.5 Use the Type S pitot tube only if the values of σ (side A) and σ (side B) are less than or equal to 0.01 and if the absolute value of the difference between $\bar{C}_p$ (A) and $\bar{C}_p$ (B) is 0.01 or less.

4.1.5 Special considerations.

4.1.5.1 Selection of calibration point.

4.1.5.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The Type S pitot coefficients so obtained, i.e., $\bar{C}_p$ (side A) and $\bar{C}_p$ (side B), will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2-6 through 2-8).

4.1.5.1.2 For Type S pitot tube-thermocouple combinations (without sample probe), select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination is used by itself or with other components in an interference-free arrangement (Figures 2-6, and 2-8).

4.1.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values (Citation 9 in Section 6). Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary. The actual blockage effect will be negligible when the theoretical blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and 3 percent or less for assemblies with external sheaths (Figure 2-10b).

4.1.5.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specification illustrated in Figure 2-6a), the value of $C_{p(s)}$ depends upon the amount of free-space between the tube and nozzle, and therefore is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or ¼ in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min (3,000 ft/min), which is the calibration velocity; note also that it is not necessary to draw an isokinetic sample during calibration (see Citation 19 in Section 6).

4.1.5.3 For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side which will face the flow). The pitot tube must still meet the alignment specifications of Figure 2-2 or 2-3, however, and must have an average deviation (σ) value of 0.01 or less (see Section 4.1.4.4).

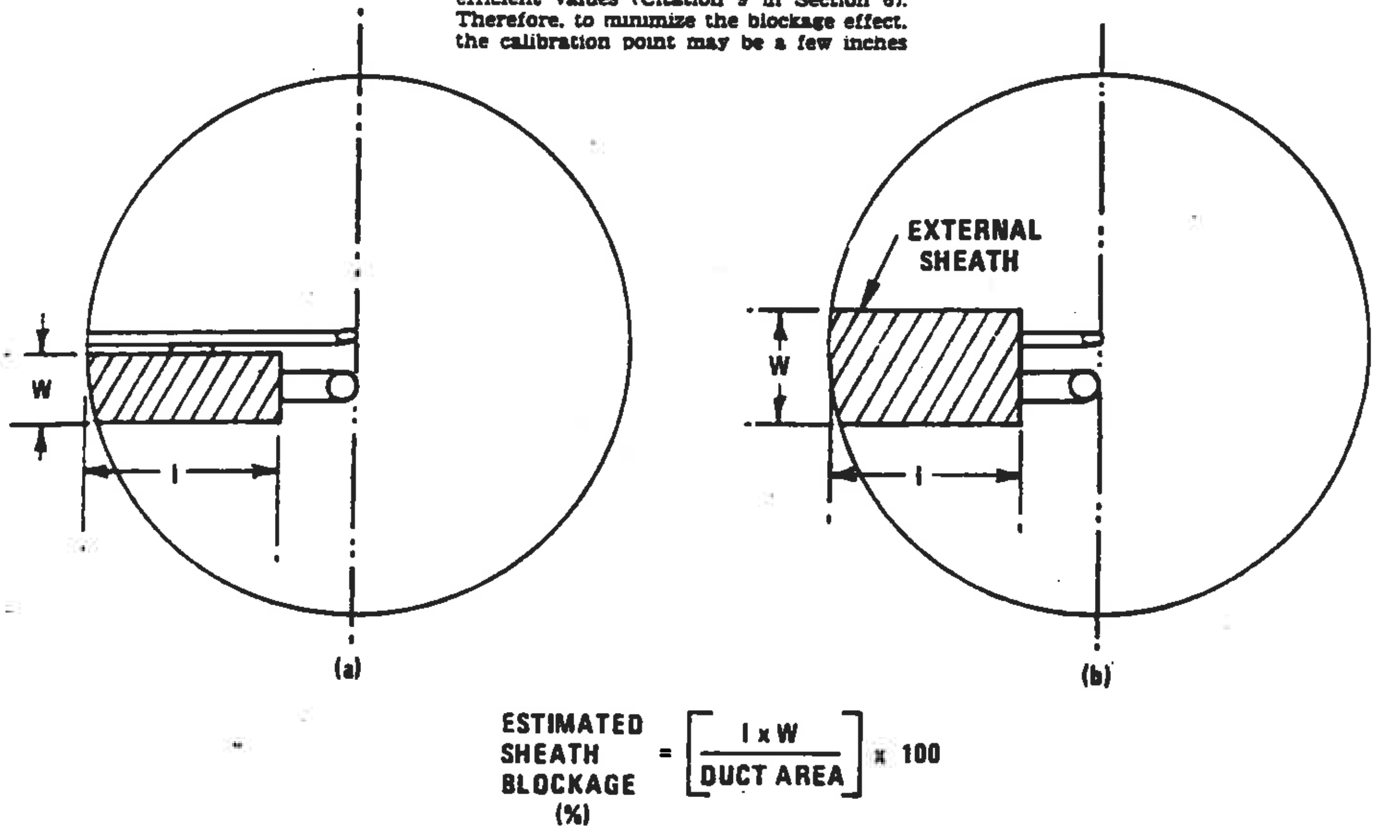


Figure 2-10. Projected-area models for typical pitot tube assemblies.

Figure 2-10. Projected-area models for typical pitot tube assemblies.

4.1.6 Field Use and Recalibration.

4.1.6.1 Field Use.

4.1.6.1.1 When a Type S pitot tube (isolated tube or assembly) is used in the field, the appropriate coefficient value (whether assigned or obtained by calibration) shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A side coefficient shall be used when the A side of the tube faces the flow, and the B side coefficient shall be used when the B side faces the flow; alternatively, the arithmetic average of the A and B side coefficient values may be used, irrespective of which side faces the flow.

4.1.6.1.2 When a probe assembly is used to sample a small duct (12 to 36 in. in diameter), the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of $C_{p(s)}$. Consult Citation 9 in Section 6 for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches (Citation 16 in Section 6).

4.1.6.2 Recalibration.

4.1.6.2.1 Isolated Pitot Tubes. After each field use, the pitot tube shall be carefully reexamined in top, side, and end views. If the pitot face openings are still aligned within the specifications illustrated in Figure 2-2 or 2-3, it can be assumed that the baseline coefficient of the pitot tube has not changed. If, however, the tube has been damanged to the extent that it no longer meets the specifications of Figure 2-2 or 2-3, the damage shall either be repaired to restore proper alignment of the face openings or the tube shall be discarded.

4.1.6.2.2 Pitot Tube Assemblies. After each field use, check the face opening alignment of the pitot tube, as in Section 4.1.6.2.1; also, remeasure the intercomponent spacings of the assembly. If the intercomponent spacings have not changed and the face opening alignment is acceptable, it can be assumed that the coefficient of the assembly has not changed. If the face opening alignment is no longer within the specifications of Figures 2-2 or 2-3, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the intercomponent spacings have changed, restore the original spacings or recalibrate the assembly.

4.2 Standard pitot tube (if applicable). If a standard pitot tube is used for the velocity traverse, the tube shall be constructed according to the criteria of Section 2.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly, the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

4.3 Temperature Gauges. After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other gauges at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405° C (761° F), use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference; alternatively, either a reference thermocouple and potentiometer (calibrated by NBS) or thermometric fixed points, e.g., ice bath and boiling water (corrected for barometric pressure) may be used. For temperatures above 405° C (761° F), use an NBS-calibrated reference thermocouple-potentiometer system or an alternate reference, subject to the approval of the Administrator.

If, during calibration, the absolute temperatures measured with the gauge being calibrated and the reference gauge agree within 1.5 percent, the temperature data taken in the field shall be considered valid. Otherwise, the pollutant emission test shall either be considered invalid or adjustments (if appropriate) of the test results shall be made, subject to the approval of the Administrator.

4.4 Barometer. Calibrate the barometer used against a mercury barometer.

5. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

5.1 Nomenclature.

A = Cross-sectional area of stack, m² (ft²).

B_{ws} = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume.

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant,

$$34.97\ \frac{m}{sec}\left[\frac{(g/g\text{-mole})(mm\ Hg)}{(°K)(mm\ H_2O)}\right]^{1/2}$$

for the metric system and

$$85.49\ \frac{ft}{sec}\left[\frac{(lb/lb\text{-mole})(in.\ Hg)}{(°R)(in.\ H_2O)}\right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack gas, dry basis (see Section 3.6) g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).

$= M_d(1-B_{ws}) + 18.0\ B_{ws}$

Equation 2-5

P_{bar} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_g = Stack static pressure, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

$= P_{bar} + P_g$

Equation 2-6

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

t_s = Stack temperature, °C (°F).

T_s = Absolute stack temperature, °K, (°R).

$= 273 + t_s$ for metric

Equation 2-7

$= 460 + t_s$ for English

Equation 2-8

T_{std} = Standard absolute temperature, 293 °K (528° R)

v_s = Average stack gas velocity, m/sec (ft/sec).

Δp = Velocity head of stack gas, mm H₂O (in. H₂O).

3,600 = Conversion factor, sec/hr.

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

5.2 Average stack gas velocity.

$$v_s = K_p C_p (\sqrt{\Delta p})_{avg} \sqrt{\frac{T_{s(avg)}}{P_s M_s}}$$

Equation 2-9

5.3 Average stack gas dry volumetric flow rate.

$$Q_{sd} = 3{,}600(1 - B_{ws}) v_s A \left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right)$$

Equation 2-10

"To convert Q_{sd} from dscm/hr (dscf/hr) to dscm/min (dscf/min), divide Q_{sd} by 60."

6. *Bibliography*

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METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, OXYGEN, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. *Principle and Applicability*

1.1 Principle. A gas sample is extracted from a stack, by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO_2), percent oxygen (O_2), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite [1] analyzer may be used for the analysis; for excess air or emission rate correction factor determination, an Orsat analyzer must be used.

1.2 Applicability. This method is applicable for determining CO_2 and O_2 concentrations, excess air, and dry molecular weight of a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, CO, and nitrogen (N_2) are not present in concentrations sufficient to affect the results.

Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) a multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air; (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator, U.S. Environmental Protection Agency.

2. *Apparatus*

As an alternative to the sampling apparatus and systems described herein, other sampling systems (e.g., liquid displacement) may be used provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are otherwise capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials inert to O_2, CO_2, CO, and N_2 and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.2 Pump. A one-way squeeze bulb, or equivalent, is used to transport the gas sample to the analyzer.

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. A probe such as that described in Section 2.1.1 is suitable.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser that will not remove O_2, CO_2, CO, and N_2, may be used to remove excess moisture which would interfere with the operation of the pump and flow meter.

2.2.3 Valve. A needle valve is used to adjust sample gas flow rate.

2.2.4 Pump. A leak-free, diaphragm-type pump, or equivalent, is used to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter. The rotameter, or equivalent rate meter, used should be capable of measuring flow rate to within ±2 percent of the selected flow rate. A flow rate range of 500 to 1000 cm^3/min is suggested.

2.2.6 Flexible Bag. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and time length of the test run, may be used. A capacity in the range of 55 to 90 liters is suggested.

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O) and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 30 cm (12 in.) is used for the flexible bag leak-check.

2.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm Hg (30 in. Hg) is used for the sampling train leak-check.

2.3 Analysis. For Orsat and Fyrite analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

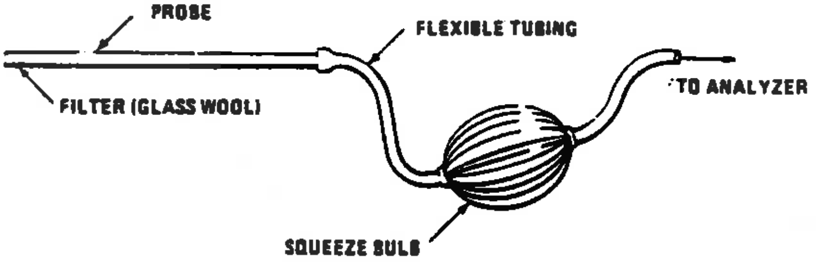

Figure 3-1. Grab-sampling train.

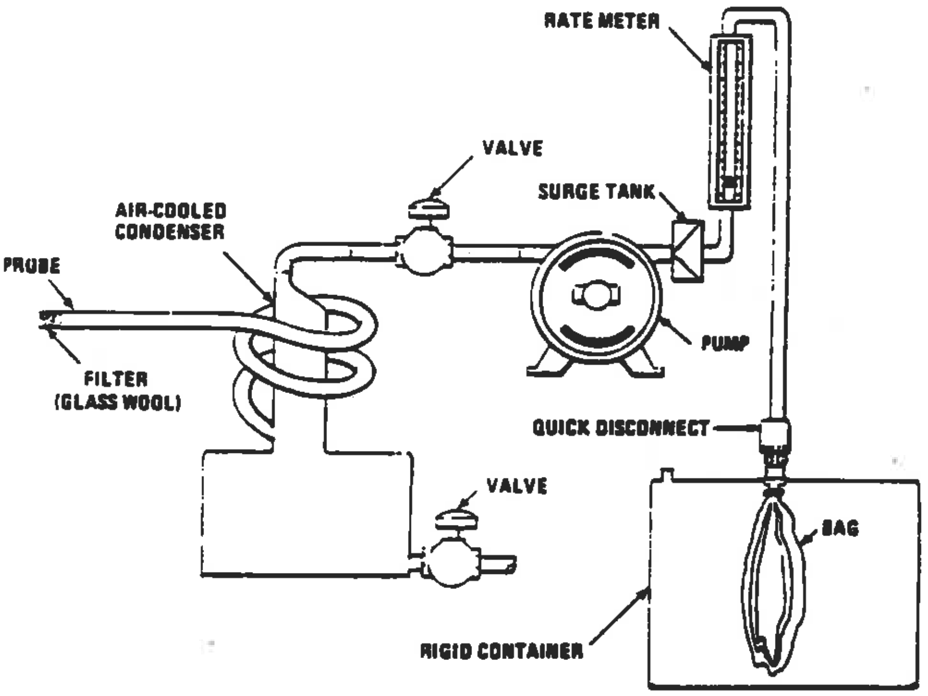

Figure 3-2. Integrated gas-sampling train.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.3.1 Dry Molecular Weight Determination. An Orsat analyzer or Fyrite type combustion gas analyzer may be used.

2.3.2 Emission Rate Correction Factor or Excess Air Determination. An Orsat analyzer must be used. For low CO_2 (less than 4.0 percent) or high O_2 (greater that 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions.

3. *Dry Molecular Weight Determination*

Any of the three sampling and analytical procedures described below may be used for determining the dry molecular weight.

3.1 Single-Point, Grab Sampling and Analytical Procedure.

3.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. If and Orsat analyzer is used, it is recommended that the analyzer be leaked-checked by following the procedure in Section 5; however, the leak-check is optional.

3.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer and immediately analyze it for percent CO_2 and percent O_2. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.1.4 Repeat the sampling, analysis, and calculation procedures, until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure.

3.2.1 The sampling point in the duct shall be located as specified in Section 3.1.1.

3.2.2 Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

3.2.3 Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft^3) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO_2 and percent O_2 using either an Orsat analyzer or a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leak-check described in Section 5 be performed before this determination; however, the check is optional. Determine the percentage of the gas that is N_2 and CO by subtracting the sum of the percent CO_2 and percent O_2 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.2.5 Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

3.3 Multi-Point, Integrated Sampling and Analytical Procedure.

3.3.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Administrator.

3.3.2 Follow the procedures outlined in sections 3.2.2 throught 3.2.5, except for the following: traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

4. *Emission Rate Correction Factor or Excess Air Determination*

NOTE: A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determination, unless approved by the Administrator. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator.

4.1 Single-Point, Grab Sampling and Analytical Procedure.

4.1.1 The sampling point in the duct shall either be at the centroid of the cross-section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

4.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. Leak-check the Orsat analyzer according to the procedure described in Section 5. This leak-check is mandatory.

FIGURE 3-3—SAMPLING RATE DATA

Time	Traverse pt.	Q lpm	% dev.*
Average			

*% Dev. $=(Q-Q_{avg})/Q_{avg} \times 100$ (Must be $\leq |10\%|$)

4.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO_2 or percent O_2. If excess air is desired, proceed as follows: (1) immediately analyze the sample as in Sections 4.1.4 and 4.1.5, for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2, and percent CO from 100 percent; and (3) calculate percent excess air as outlined in Section 6.2.

4.1.4 To insure complete absorption of the CO_2, O_2, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.

NOTE: Since this single-point, grab sampling and analytical procedure in normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Section 4.4 be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure.

4.2.1 The sampling point in the duct shall be located as specified in Section 4.1.1.

4.2.2 Leak-check (mandatory) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of a least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum shall remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

4.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 30 liters (1.00 ft^3) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-check (see Section 5) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2, and percent CO from 100 percent; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5 To insure complete absorption of the CO_2, O_2, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three of four) should be make between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.2.6 Repeat the analysis until the following criteria are met:

4.2.6.1 For percent CO_2, repeat the analytical procedure until the results of any three analyses differ by no more that (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent or (b) 0.2 percent by volume when CO_2 is less than or equal to 4.0 percent. Average the three acceptable values of percent CO_2 and report the results to the nearest 0.1 percent.

4.2.6.2 For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2 and report the results to the nearest 0.1 percent.

4.2.6.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO and report the results to the nearest 0.1 percent.

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before an after the analysis.

NOTE: Although in most instances only CO_2 or O_2 is required, it is recommenued that both CO_2 and O_2 be measured, and that Section 4.4.1 be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure.

4.3.1 Both the minimum number of sampling points and the sampling point location shall be as specified in Section 3.3.1 of this method. The use of fewer points than specified is subject to the approval of the Administrator.

4.3.2 Follow the procedures outlined in Sections 4.2.2 through 4.2.7, except for the following: Traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

4.4 Quality Control Procedures.

4.4.1 Data Validation When Both CO_2 and O_2 Are Measured. Although in most instances, only CO_2 or O_2 measurement is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The following quality control procedure is suggested.

NOTE: Since the method for validating the CO_2 and O_2 analyses is based on combustion of organic and fossil fuels and dilution of the gas stream with air, this method does not apply to sources that (1) remove CO_2 or O_2 through processes other than combustion, (2) add O_2 (e.g., oxygen enrichment) and N_2 in proportions different from that of air, (3) add CO_2 (e.g., cement or lime kilns), or (4) have no fuel factor, F_o, values obtainable (e.g., extremely variable waste mixtures). This method validates the measured proportions of CO_2 and O_2 for the fuel type, but the method does not detect sample dilution resulting from leaks during or after sample collection. The method is applicable for samples collected downstream of most lime or limestone flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F_o check minimally useful.

4.4.1.1 Calculate a fuel factor, F_o, using the following equation:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2}$$

Eq. 3-3

Where:

$\%O_2$ = Percent O_2 by volume (dry basis).

$\%CO_2$ = Percent CO_2 by volume (dry basis).

20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as follows:

$$\%CO_2(adj) = \%CO_2 + \%CO$$

$$\%O_2(adj) = \%O_2 - 0.5\ \%CO$$

Where: %CO = Percent CO by volume (dry basis).

4.4.1.2 Compare the calculated F_o factor with the expected F_o values. The following table may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combination, calculate the combined fuel F_d and F_c factors (as defined in Method 19) according to the procedure in Method 19 Section 5.2.3. Then calculate the F_o factor as follows:

$$F_o = \frac{0.209\ F_d}{F_c}$$

Eq. 3-4

Fuel type	F_o range
Coal:	
Anthracite and lignite	1.016–1.130
Bituminous	1.083–1.230
Oil:	
Distillate	1.260–1.413
Residual	1.210–1.370
Gas:	
Natural	1.600–1.836
Propane	1.434–1.586
Butane	1.405–1.553
Wood	1.000–1.120
Wood bark	1.003–1.130

Calculated F_o values beyond the acceptable ranges shown in this table should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should be reviewed and verified. An acceptability range of ±12 percent is appropriate for the F_o factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate, i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time-consuming and costly.

5. *Leak-Check Procedure for Orsat Analyzers*

Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be throughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak-checking an Orsat analyzer is:

5.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

5.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

5.1.3 Record the meniscus position.

5.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

5.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met.

5.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

5.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

5.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned, and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

6. *Calculations*

6.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

%EA = Percent excess air.

$\%CO_2$ = Percent CO_2 by volume (dry basis).

$\%O_2$ = Percent O_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

$\%N_2$ = Percent N_2 by volume (dry basis).

0.264 = Ratio of O_2 to N_2 in air, v/v.

0.280 = Molecular weight of N_2 or CO, divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

6.2 Percent Excess Air. Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O_2, CO, and N_2 (obtained from Section 4.1.3 or 4.2.4) into Equation 3-1.

$$\%\ EA = \frac{\%O_2 - 0.5\%\ CO}{0.264\%\ N_2 - (\%O_2 - 0.5\ \%\ CO)} \times 100$$

Equation 3-1

NOTE: The equation above assumes that ambient air is used as the source of O_2 and that the fuel does not contain appreciable amounts of N_2 (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil, and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternate methods, subject to approval of the Administrator, are required.

6.3 Dry Molecular Weight. Use Equation 3-2 to calculate the dry molecular weight of the stack gas

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$$

Equation 3-2

NOTE: The above equation does not consider argon in air (about 0.9 percent, moleculars weight of 37.7). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Administrator.

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METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 120±14° C (248±25° F) or such other temperature as specified by an applicable subpart of the standards or approved by Administrator. U.S. Environmental Protection Agency, for a particular application. The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. *Apparatus*

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Bibliography); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Bibliography). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be <30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (⅛ to ½ in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480° C (900° F) quartz liners shall be used for temperatures between 480 and 900° C (900 and 1,650° F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820° C (1,508° F), and for quartz it is 1,500° C (2,732° F).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[1] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

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[1] Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

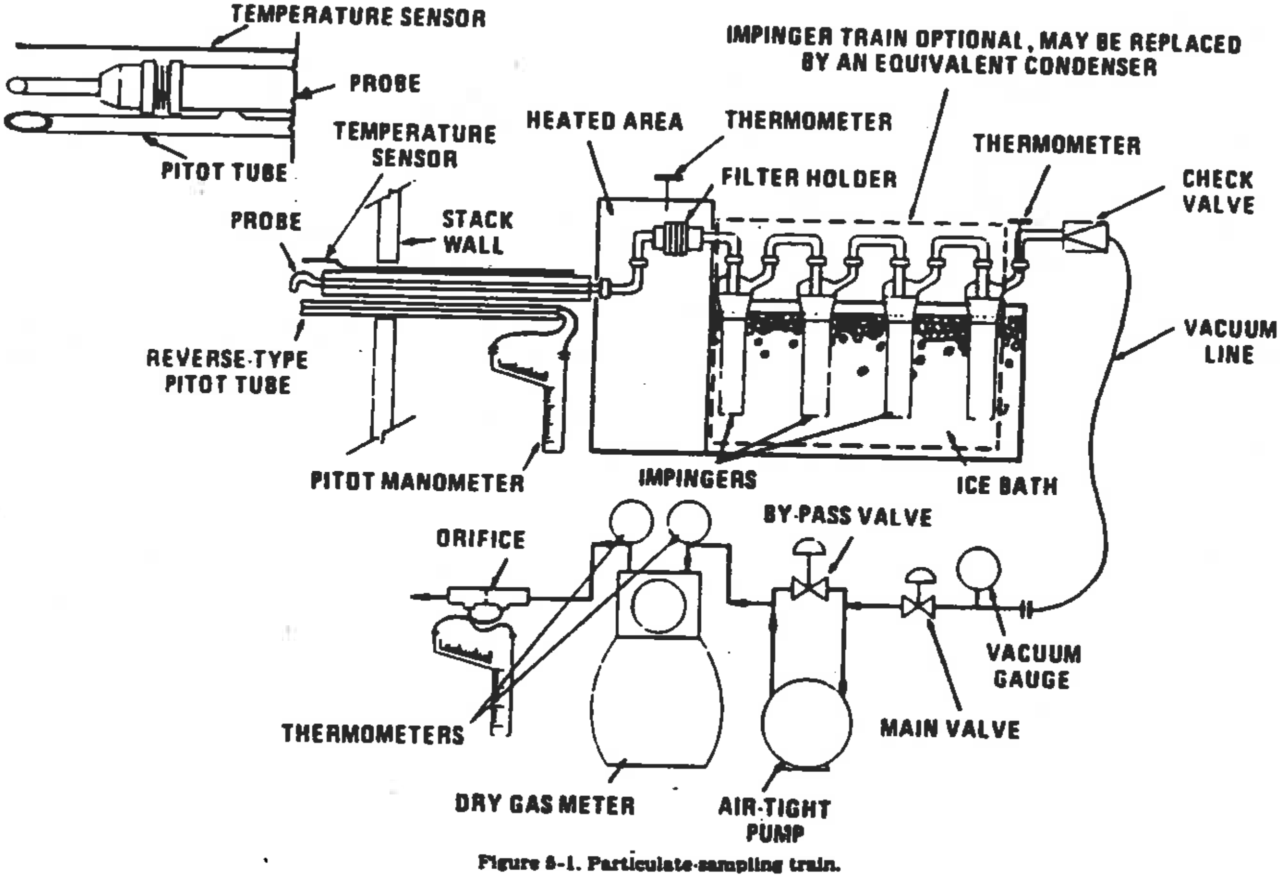

Figure 5-1. Particulate-sampling train.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used or velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, it used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD–0581 may be used.

2.1.7 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperture to within 1° C (2° F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample has stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20° C (68° F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that decribed in APTD–0581 or APDT–0576 may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

2.2 Sample Recovery. The following items are needed.

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable or use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container: not

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.2 Analysis. For analysis, the following equipment is needed.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. *Reagents*

3.1 Sampling. The reagents used in sampling are as follows:

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986–71 (Reapproved 1978) (incorporated by reference—see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Citation 10 in Section 7 Bibliography, may be used to select the appropriate filter.

3.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Water. When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

le Recovery. Acetone-reagent percent residue, in glass bot- ired. Acetone from metal con- nerally has a high residue blank ould not be used. Sometimes, suppli- transfer acetone to glass bottles from etal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. *Procedure*

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD-0576.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260° C (500° F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cycone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve, completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass value; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes unecessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered;

If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leakcheck shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered.

If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85±0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29±4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges do not use the nomographs unless appropriate steps (see Citation 7 in Bibliography) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block the openings around the probe and portho to prevent unrepresentative dilution of th gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack wall[illegible]hen sampling near the walls or when r[illegible]ng or inserting the probe through th[illegible]rtholes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20° C (68° F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see Section 4.1.4.2). The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

FIGURE 5-2—PARTICULATE FIELD DATA

Plant ....
Location ....
Operator ....
Date ....
Run No ....
Sample box No ....
Meter box No ....
Meter ΔH@ ....
C factor ....
Pitot tube coefficient, Cp ....

SCHEMATIC OF STACK CROSS SECTION

Ambient temperature ....
Barometric pressure ....
Assumed moisture, % ....
Probe length, m (ft.) ....
Nozzle identification No. ....
Average calibrated nozzle diameter, cm (in.) ....
Probe heater setting ....
Leak rate, m^3/min, (cfm) ....
Probe liner material ....
Static pressure, mm. Hg (in. Hg) ....
Filter No. ....

Traverse point number	Sampling time	Vacuum	Stack temperature	Velocity head	Pressure differential across orifice meter	Gas sample volume	Gas sample temperature at dry gas meter		Filter holder temperature	Temperature of gas leaving condenser or last impinger
							Inlet	Outlet		
	(θ), min.	mm Hg (in. Hg)	(T_s), °C (° F)	(ΔP_s), mm (in.) H_2O	mm H_2O (in. H_2O)	m^3 (ft^3)	°C (° F)	° C (° F)	° C (° F)	° C (° F)
Total							Avg.	Avg.		—
Average							Avg.			—

Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid on transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contaminations.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occured during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Note, Section 2.1.7).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

FIGURE 5-3—ANALYTICAL DATA

Plant ____________________
Date ____________________
Run No. ____________________
Filter No. ____________________
Amount liquid lost during transport ________
Acetone blank volume, ml __________
Acetone wash volume, ml __________
Acetone blank concentration, mg/mg (equation 5-4) __________
Acetone wash blank, mg (equation 5-5) ________

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gai
1.______			
2.______			
Total ______			
Less acetone blank ______			
Weight of particulate matter ______			

	Volume of liquid water collecte	
	Impinger volume, ml	Silica gel weight, g
Final ______		
Initial ______		
Liquid collected ______		
Total volume collected ______		g* ml

*Convert weight of water to volume by dividing total weig increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\ \text{g/ml})} = \text{Volume water, ml}$$

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at 105° C (220° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at 105° C (220° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumentrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

4.4 Quality Control Procedures. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional for the tester.

4.4.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 5.3, determine the $\Delta H_@$ for the metering system orifice. The $\Delta H_@$ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528°R and 29.92 in. Hg. The $\Delta H_@$ is calculated as follows:

$$\Delta H_@ = 0.0319\ \Delta H\ \frac{T_m}{P_{bar}}\ \frac{\Theta^2}{Y^2 V_m^2}$$

Eq. 5-9

Where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.

T_m = Absolute average dry gas meter temperature, °R.

P_{bar} = Barometric pressure, in. Hg.

Θ = Total sampling time, min.

Y = Dry gas meter calibration factor, dimensionless.

V_m = Volume of gas sample as measured by dry gas meter, dcf.

$0.0319 = (0.0567\ \text{in. Hg}/°\text{R}) \times (0.75\ \text{cfm})^2$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the $\Delta H_@$ pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperature, and the barometric pressure. Calculate a dry gas meter calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\left[\frac{0.0319\ T_m}{P_{bar}}\right]^{1/2}$$

Eq. 5-10

Where:

Y_c = Dry gas meter calibration check value, dimensionless.

10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that:

$$0.97Y < Y_c < 1.03Y$$

If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

4.4.2 Calibrated Critical Orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box may be used as a quality control check by following the procedure of Section 7.2.

5. *Calibration*

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 01.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System.

5.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5.5. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev). A spirometer of 400 liters (14 ft³) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the dry gas meter. Also note the barometric pressure, and the temperatures of the wet test meter, the inlet of the dry gas meter, and the outlet of the dry gas meter. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m³ (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5.6, and calculate Y, the dry gas meter calibration factor, and $\Delta H_@$, the orifice calibration factor, at each orifice setting as shown on Figure 5.6. Allowable tolerances for individual Y and $\Delta H_@$ values are given in Figure 5.6. Use the average of the Y values in the calculations in Section 6.

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divided the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

5.3.2 Calibration After Use. After each filed use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, inset a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the dry gas meter calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as previously detailed.

Alternative procedures, e.g., rechecking the orifice meter coefficient may be used, subject to the approval of the Administrator.

5.3.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field.

Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical simple flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The follow-

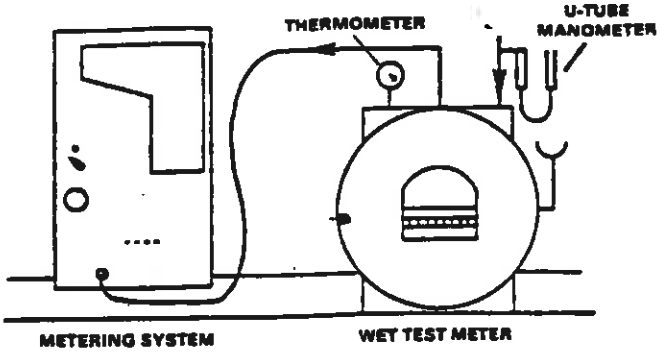

Figure 5.5 Equipment arrangement for metering system calibration.

Date______________ Metering System Identification:______________

Barometric pressure, P_b = ______ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume (V_w) ft³	Dry gas meter volume (V_m) ft³	Temperatures				Time (θ) min
			Spirometer (wet meter) (t_w) °F	Dry Gas Meter			
				Inlet (t_i) °F	Outlet (t_o) °F	Average (t_m) °F	

Calculations

ΔH in. H_2O	Y $\frac{V_w P_b (t_m + 460)}{V_m(P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	ΔH@ $\frac{0.0317 \Delta H}{P_b (t_o + 460)} \left[\frac{(t_w + 460) \theta}{V_w}\right]^2$
Average		

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ±0.02 from average.

ΔH@ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ±0.20 from average.

Figure 5.6. Example data sheet for calibration of metering system (English units).

ing procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

6.1 Nomenclature

A_n = Cross-sectional area of nozzle, m² (ft²).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
I = Percent of isokinetic sampling.
L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.0057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.
L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i=1, 2, 3....n), m³/min (cfm).
L_p = Leakage rate observed during the post-test leak check, m³/min (cfm).
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0lb/lb-mole).
m_a = Mass of residue of acteone after evaporation, mg.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 mm Hg-m °K-g-mole (21.85 in. Hg-ft³/°R-lb-mole)
T_m = Absolute average dry gas meter temp ature (see Figure 5-2), °K (°R).
T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).
T_{std} = Standard absolute temperature, 293° K (528° R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dscf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
Y = Dry gas meter calibration factor.
ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).

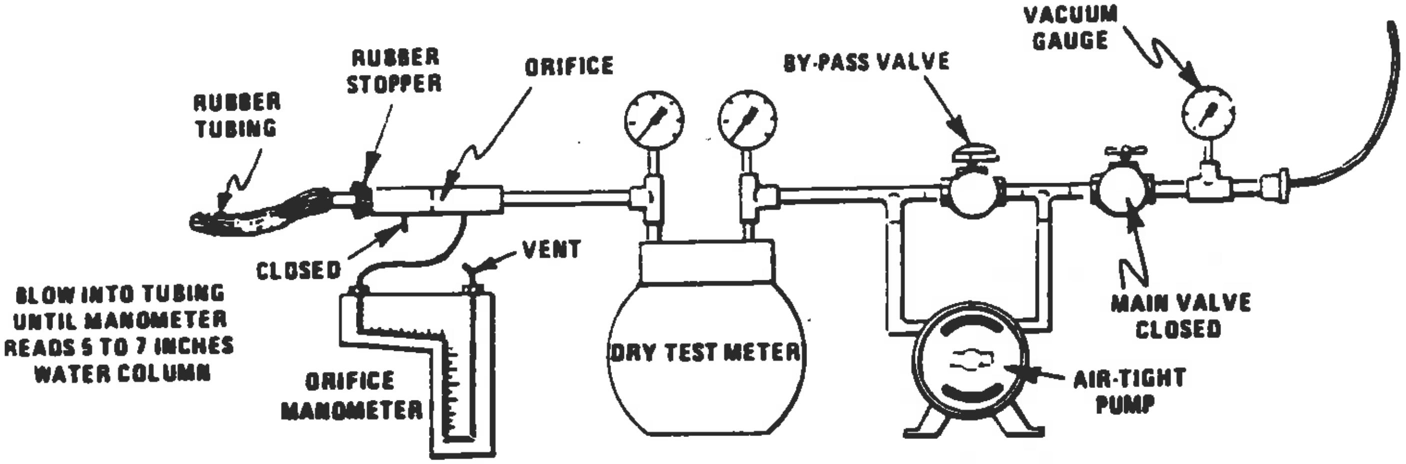

Figure 5-4. Leak check of meter box.

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).
θ = Total sampling time, min.
θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.
θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
13.6 = Specific gravity of mercury.
60 = Sec/min.
100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(std)} = V_m Y\left(\frac{T_{std}}{T_m}\right)\left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right] = K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation 5-1

where:
K_1 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

NOTE: Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 with the expression:

$$V_m - (L_p - L_a)\theta$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$\left[V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_i - (L_p - L_a)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

6.4 Volume of water vapor.

Equation 5-2

$$V_{w(std)} = V_{lc}\left(\frac{\rho_w}{M_w}\right)\left(\frac{R T_{std}}{P_{std}}\right) = K_2 V_{lc}$$

where:
K_2 = 0.001333 m³/ml for metric units
= 0.04707 ft³/ml for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

Equation 5-3

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1° C (2° F).

6.6 Acetone Blank Concentration.

Equation 5-4

$$C_a = \frac{m_a}{V_a \rho_a}$$

6.7 Acetone Wash Blank.

$W_a = C_a V_{aw} \rho_a$ Equation 5-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3).

NOTE: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

C_s = (0.001 g/mg) ($m_n/V_{m(std)}$) Equation 5-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m³	0.02832.
g/ft³	gr/ft³	15.43.
g/ft³	lb/ft³	2.205 x 10⁻³.
g/ft³	g/m³	35.31.
g	mg	0.001

6.11 Isokinetic Varition.

6.11.1 Calculation From Raw Data.

$$I = \frac{100\, T_s[K_3 V_{lc} + (V_m Y/T_m)(P_{bar} + \Delta H/13.6)]}{60\theta v_s P_s A_n}$$

Equation 5-7

where:
K_3 = 0.003454 mm Hg−m³/ml−°K for metric units.
= 0.002669-in. Hg−ft³/ml−°R for English units.

6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60(1-B_{ws})} = K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

Equation 5-8

where:
K_4 = 4.320 for metric units
= 0.09450 for English units.

6.12 Acceptable Results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the particulate results are low in comparison to the standard, and I is over 110 percent or less than 90 percent, the Administrator may accept the results. Citation 4 in the bibliography section can be used to make acceptability judgments. If I is judeged to be unacceptable, reject the particulate results and repeat the test.

6.13 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 5.2 and 5.3 of Method 2.

7. *Alternative Procedures*

7.1 Dry Gas Meter as a Calibration Standard. A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 5.3, provided that it is calibrated initially and recalibrated periodically as follows:

7.1.1 Standard Dry Gas Meter Calibration.

7.1.1.1 The dry gas meter to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity, e.g., 3 liters/rev (0.1 ft³/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev) and capable of measuring volume to within ±1.0 percent; wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

7.1.1.2 Set up the components as shown in Figure 5.7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the dry gas meter should be minimized [no greater than 100 mm H₂O (4 in. H₂O) at a flow rate of 30 liters/min (1 cfm)]. This can be accomplished by using large diameter tubing connections and straight pipe fittings.

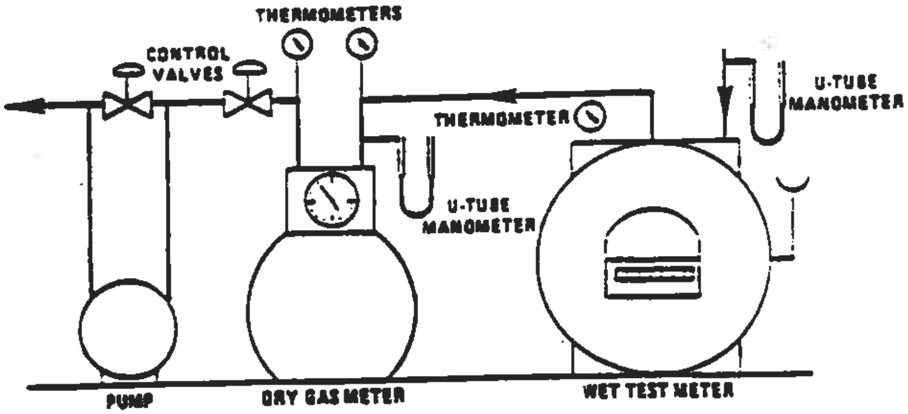

Figure 5.7 . Equipment arrangement for dry-gas meter calibration.

7.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

DATE:____________________

DRY GAS METER IDENTIFICATION:____________________

BAROMETRIC PRESSURE (P_b):____________________ in. Hg

APPROXIMATE FLOW RATE ($\tilde{Q}$) cfm	SPIROMETER (WET METER) GAS VOLUME (V_s) ft³	DRY GAS METER VOLUME (V_{dg}) ft³	TEMPERATURES				DRY GAS METER PRESSURE (Δp) in. H₂O	TIME (Θ) min.	FLOW RATE (Q) cfm	METER METER COEFFICIENT (Y_{ds})	AVERAGE METER COEFFICIENT ($\bar{Y}_{ds}$)
			SPIROMETER (WET METER) (t_s) °F	DRY GAS METER							
				INLET (t_i) °F	OUTLET (t_o) °F	AVERAGE ($\bar{t}_d$) °F					
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = 17.65 \cdot \frac{V_s}{\Theta} \cdot \frac{P_b}{(t_s + 460)}$$

$$Y_{ds} = \frac{V_s}{V_{dg}} \cdot \frac{(\bar{t}_d + 460)}{(t_s + 460)} \cdot \frac{P_b}{(P_b + \frac{\Delta p}{13.6})}$$

Figure 5.8. Example data sheet for calibration of a standard dry gas meter for method 5 sampling equipment (English units).

7.1.1.4 Calculate flow rate, Q, for each run using the wet test meter gas volume, V_w, and the run time, θ. Calculate the dry gas meter coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar}}{t_w + t_{std}} \frac{V_w}{\theta}$$

$$Y_{ds} = \frac{V_w}{V_{ds}} \frac{(t_{ds} + t_{std})}{(t_w + t_{std})} \frac{P_{bar}}{\left(P_{bar} + \frac{\Delta p}{13.6}\right)}$$

Where:

K_1 = 0.3858 for international system of units (SI): 17.64 for English units.
V_w = Wet test meter volume, liters (ft ^{3}).
V_{ds} = Dry gas meter volume, liters (ft ^{3}).
t_{ds} = Average dry gas meter temperature, °C (°F).
t_{std} = 273° C for SI units; 460° F for English units.
t_w = Average wet test meter temperature, °C (°F).
P_{bar} = Barometric pressure, mm Hg (in. Hg).
Δp = Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).
θ = Run time, min.

7.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in five average meter coefficients, $\overline{Y}_{ds}$.

7.1.1.6 Prepare a curve of meter coefficient, $\overline{Y}_{ds}$ versus flow rate, Q, for the dry gas meter. This curve shall be used as a reference when the meter is used to calibrate other dry gas meters and to determine whether recalibration is required.

7.1.2 Standard Dry Gas Meter Recalibration.

7.1.2.1 Recalibrate the standard dry gas meter against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard dry gas meter is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

7.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 28 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within ±1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

7.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in Section 5.3, provided that they are selected, calibrated, and used as follows:

7.2.1 Section of Critical Orifices.

7.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices; i.e., a critical vacuum can be obtained, as described in Section 7.2.2.2.3. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range.

A minimum of three critical orifices will be needed to calibrate a Method 5 dry gas meter (DGM); the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown below give the following approximate flow rates:

Gauge/cm	Flow rate (liters/min)	Gauge/cm	Flow rate (liters/min)
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

7.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13- by 20-mm sleeve type, into a ½-inch Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-6.

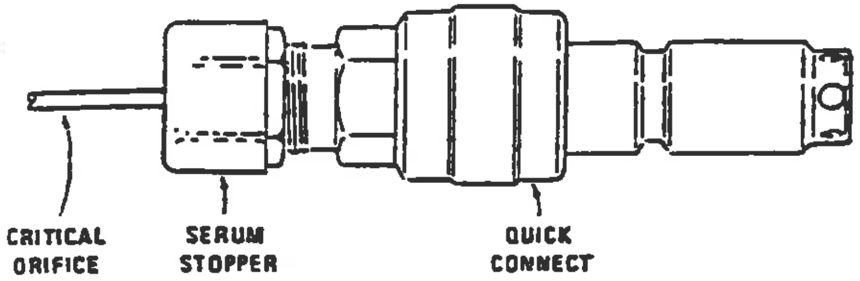

Figure 5-9. Critical orifice adaptation to Method 5 metering system.

7.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in Section 2.1.8 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

7.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used: i.e., there should be no connections to the inlet of the orifice.

7.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then trun on the pump, and determine whether there is any leakage. The leakage rate shall be zero: i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

7.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See Section 5.6 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

7.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in Section 5.3. Make sure that the wet test meter meets the requirements stated in Section 7.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

7.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5-10.

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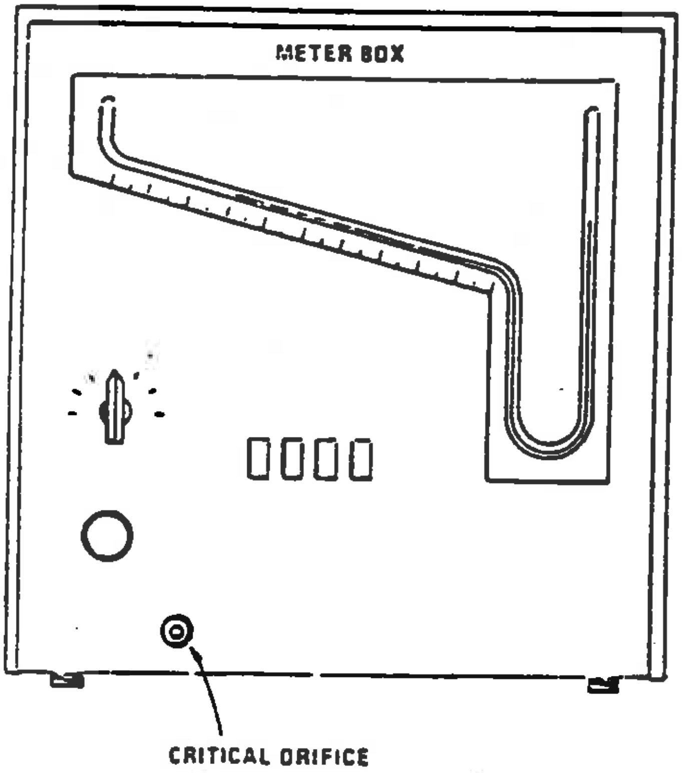

Figure 5-10. Apparatus setup.

7.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

7.2.2.2.2 Leak check the system as in Section 7.2.2.1.1. The leakage rate shall be zero.

7.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, H. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice.

Orifices that do not reach a critical value shall not be used.

7.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section 2.1.9. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

7.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of 0.00283 m³ (0.1 ft³) or in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5 percent in K'. Record the information listed in Figure 5-11.

7.2.2.2.6 Calculate K' using Equation 5-9.

Where:

$$K' = \frac{K_1 V_m Y (P_{bar} + \Delta H/13.6) \sqrt{T_{amb}}}{P_{bar} T_m \Theta}$$

Eq. 5-9

K' = Critical orifice coefficient, $\frac{(m^3)(^\circ K)^{1/2}}{(mm.\ Hg)(min)} \left[\frac{(ft^3)(^\circ R)^{1/2}}{(in.\ Hg)(min)} \right]$

T_{amb} = Absolute ambient temperature, °K (°R).

Average the K' values. The individual K' values should not differ by more than ±0.5 percent from the average.

7.2.3 Using the Critical Orifices as Calibration Standards.

7.2.3.1 Record the barometric pressure.

Date ______ Train ID ______ DGM cal. factor ______ Critical orifice ID ______

Dry gas meter		Run number 1	2
Final reading	m³ (ft³)		
Initial reading	m³ (ft³)		
Difference, V_m	m³ (ft³)		
Inlet/Outlet temperatures:			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. Temperature, t_m	°C (°F)		
Time, Θ	min/sec	/	/
	min		
Orifice man. rdg., ΔH	mm (in.) H_2O		
Bar. pressure, P_{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
K' factor			
Average			

Figure 5-11. Data sheet for determining K' factor.

7.2.3.2 Calibrate the metering system according to the procedure outlined in Sections 7.2.2.2.1 to 7.2.2.2.5. Record the information listed in Figure 5.12.

7.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_m(std) = K_1 V_m \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Eq. 5-10

$$V_{cr}(std) = K' \frac{P_{bar} \Theta}{\sqrt{T_{amb}}}$$

Eq. 5-11

$$Y = \frac{V_{cr(std)}}{V_{m(std)}}$$

Eq. 5-12

where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dsm³ (dscf).

K_1 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

7.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

7.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to Section 7.2.2.2.

Date ______ Train ID ______ Critical orifice ID ______ Critical orifice K' factor ______

Dry gas meter		Run number 1	2
Final reading	m³ (ft³)		
Initial reading	m³ (ft³)		

Dry gas meter		Run number 1	Run number 2
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures			
Initial	°C (°F)	/	/
Final	°C (°F)		
Avg. Temperature, t_m	°C (°F)		
Time, Θ	min/sec	/	/
	min		
Orifice man. rdg., ΔH	mm (in.) H_2O		
Bar pressure, P_{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
$V_{m(std)}$	m^3 (ft^3)		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y			

Figure 5-12. Data sheet for determining DGM Y factor.

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METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m^3 (2.12×10^{-7} lb/ft^3). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m^3 of SO_2 can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m^3.

Possible interferents are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO_2 analysis. When samples are being taken from a gas stream with high concentrations of very find metallic fumes (such as in inlets to control devices), a high-efficiency glass fiber filter must be used in place of the glass wool plug (i.e., the one in the probe) to remove the cation interferents.

Free ammonia interferes by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, U.S. Environmental Protection Agency, are required.

2. *Apparatus*

2.1 Sampling. The sampling train is shown in Figure 6-1, and component parts are discussed below. The tester has the option of substituting sampling equipment described in Method 8 in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8.

The tester also has the option of determining SO_2 simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3 percent peroxide solution, or (2) by replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO_2 must be consistent with the procedure in Method 8.

2.1.1 Probe. Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6-mm inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated outstack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers. One midget bubbler, with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

At the option of the tester, a midget impinger may be used in place of the midget bubbler.

Other collection absorbers and flow rates may be used, but are subject to the approval of the Administrator. Also, collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

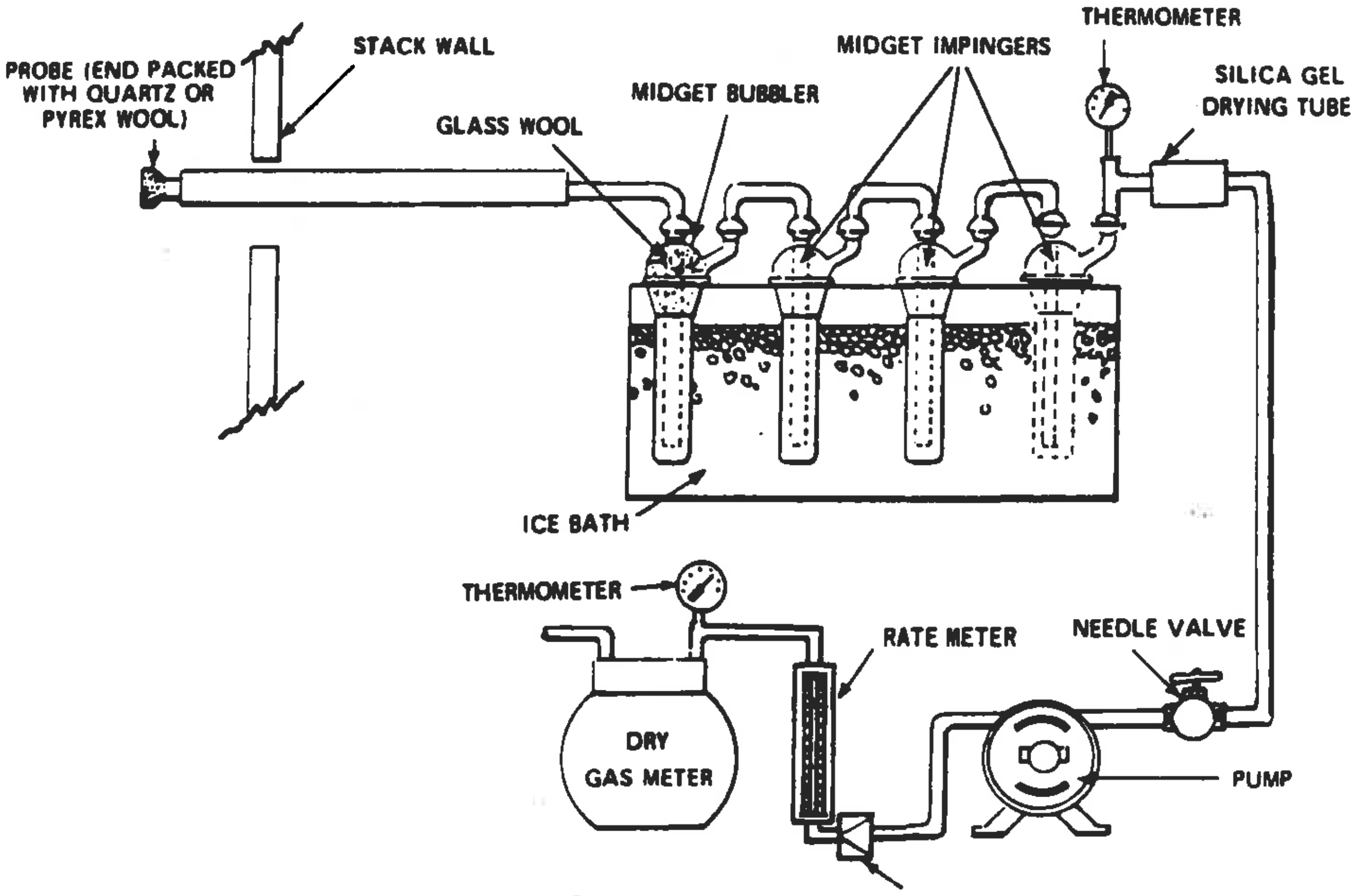

Figure 6-1. SO_2 sampling train.

2.1.3 Glass Wool. Borosilicate or quartz.

2.1.4 Stopcock Grease. Acetone-insoluble, heatstable silicone grease may be used, if necessary.

2.1.5 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1° C (2° F.)

2.1.6 Drying Tube. Tube packed with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of decissants (equivalent or better) may be used, subject to approval of the Administrator.

2.1.7 Valve. Needle valve, to regulate sample gas flow rate.

2.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9. Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min.

2.1.10 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 3° C (5.4° F).

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.12 Vacuum Gauge and Rotameter At least 760 mm Hg (30 in. Hg) gauge and 0-40 cc min rotameter, to be used for leak check of the sampling train.

2.2 Sample Recovery.

2.2.1 Wash bottles. Polyethylene or glass, 500 ml, two.

2.2.2 Storage Bottles. Polyethylene, 100 ml, to store impinger samples (one per sample).

2.3 Analysis.

2.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one per sample), and 25-ml sizes.

2.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000 ml size.

2.3.3 Burettes. 5- and 50-ml sizes.

2.3.4 Erlenmeyer Flasks. 250 ml-size (one for each sample, blank, and standard).

2.3.5 Dropping Bottle. 125-ml size, to add indicator.

2.3.6 Graduated Cylinder. 100-ml size.

2.3.7 Spectrophotometer. To measure absorbance at 352 nanometers.

3. *Reagents*

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling.

3.1.1 Water. Deionized distilled to conform to ASTM specification D1193-77, Type 3 (incorporated by reference—see § 60.17). At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 percent. Mix 80 ml of isopropanol with 20 ml of deionized, distilled water. Check each lot of isopropanol for peroxide impurities as follows: shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 352 nanometers on a spectrophotometer. If absorbance exceeds 0.1, reject alcohol for use.

Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (30 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent. Dissolve 10.0 grams KI in deionized, distilled water and dilute to 100 ml. Prepare when needed.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 80 Percent. Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.3 Analysis.

3.3.1 Water. Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 percent.

3.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium Perchlorate Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2 \cdot 3H_2O$] in 200 ml distilled water and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of [$BaCl_2 \cdot 2H_2O$] may be used instead of the perchlorate. Standardize as in Section 5.5.

3.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

3.3.6 Quality Assurance Audit Samples. Sulfate samples in glass vials prepared by EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. Each set will consist of two vials having solutions of unknown concentrations. Only whe making compliance determinations, obtain an audit sample set from the Quality Assu ance Management office at each EPA re gional Office or the responsible enforcement agency. (NOTE: The tester should notify the quality assurance office or the responsible enforcement agency at least 30 days prior to the test date to allow sufficient time for sample delivery.)

4. *Procedure*

4.1 Sampling.

4.1.1 Preparation of collection train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-check procedure. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vaccum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inle plug before turning off the pump.

It is suggested (not mandatory) that th pump be leak-checked separately, eith prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the trying tube or the pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

Other leak-check procedures may be used, subject to the approval of the Adminstrator, U.S. Environmental Protection Agency.

4.1.3 Sample collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings (dry gas meter, tempertures at dry gas meter and at impinger outlet and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperture of the gases leaving the last impinger at 20° C (68° F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak check as in Section 4.1.2 (This leak check is mandatory.) If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger with 15 ml of 3 percent H_2O_2. The tester may opt to simply use ambient air, without purification.

4.2 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with deionized, distilled water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample Analysis. Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

Note: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.

4.4 Audit Sample Analysis. Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is the Source Branch listed in Section 3.3.6.) The same analysts, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total mg SO_2/sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

The concentrations of the audit samples obtained by the analyst shall agree within 5 percent of the actual concentrations. If the 5-percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see Note in first paragraph of this section).

Failure to meet the 5-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

5. *Calibration*

5.1 Metering System.

5.1.1 Initial Calibration. Before its initial use in the field, first leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows: place a vacuum gauge at the inlet to the drying tube and pull a vaccum of 250 mm (10 in.) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vaccum shall remain stable for at least 30 seconds. Carefully release the vaccum gauge before releasing the flow meter end.

Next, remove the drying tube and calibrate the metering system (at the sampling flow rate specified by the method) as follows: connect an appropriately sized wet test meter (e.g., 1 liter per revolution) to the inlet. Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three, or more revolutions of the dry gas meter may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers.

5.3 Rotameter. The rotameter need not be calibrated but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

Run duplicate analyses. Calculate the normality using the average of a pair of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

6. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

C_{SO_2} = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dscm (lb/dscf).
N = Normality of barium perchlorate titrant, milliequivalents/ml.
P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_m = Average dry gas meter absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293° K (528° R).
V_a = Volume of sample aliquot titrated, ml.
V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.
V_t = Volume of barium perchlorate titrant used for the sample, ml (average or replicate titrations).
V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
Y = Dry gas meter calibration factor.
32.03 = Equivalent weight of sulfur dioxide.

6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K_1 Y \frac{V_m P_{bar}}{T_m}$$

Equation 6-1

where:
K_1 = 0.3858° K/mm Hg for metric units.
= 17.64° R/in. Hg for English units.

6.3 Sulfur dioxide concentration.

$$C_{SO_2} = K_2 \frac{(V_t - V_{tb})\, N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 6-2

where:
K_2 = 32.03 mg/meq. for metric units.
= 7.061×10^{-5} lb/meq. for English units.

6.4 Relative Error (RE) for QA Audit Samples, Percent.

$$RE = \frac{C_d - C_a}{C_a} \times 100 \qquad \text{Eq. 6-3}$$

Where:

C_d = Determined audit sample concentration, mg/dscm.

C_a = Actual audit sample concentration, mg/dscm.

7. *Alternative Procedures*

7.1 Dry Gas Meter as a Calibration Standard. A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 5.1, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, Section 7.1, with the following exception: (1) the dry gas meter is calibrated against a wet test meter having a capacity of 1 liter/rev or 3 liters/rev and having the capability of measuring volume to within ±1 percent; (2) the dry gas meter is calibrated at 1 liter/min (2 cfh); and (3) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

7.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the dry gas meter specified in Section 2.1.10, provided that it is selected, calibrated, and used as follows:

7.2.1 **Preparation of Collection Train.** Prepare the sampling train as shown in Figure 6-2. The rotameter and surge tank are optional but are recommended in order to detect changes in the flow rate.

Note.—The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6-3.

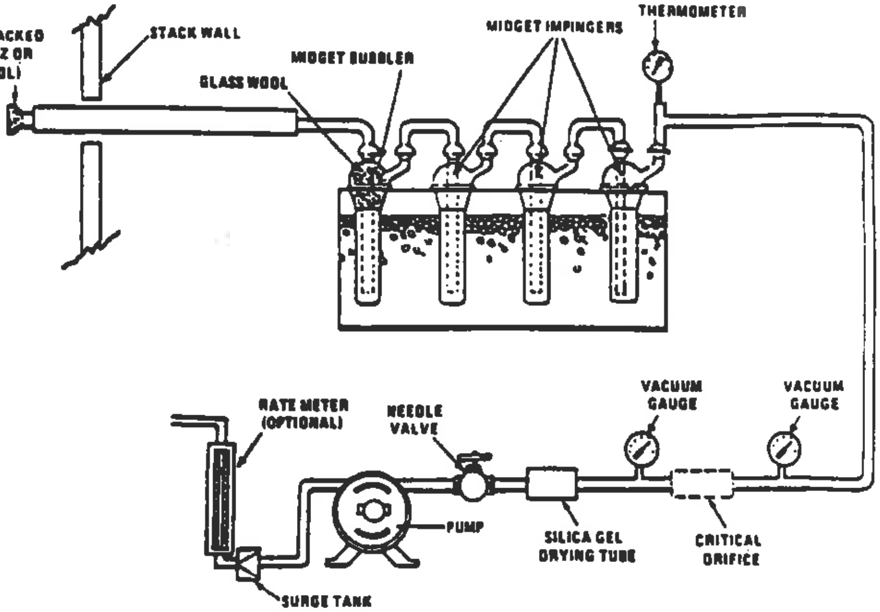

Figure 6-2. SO_2 sampling train using a critical orifice.

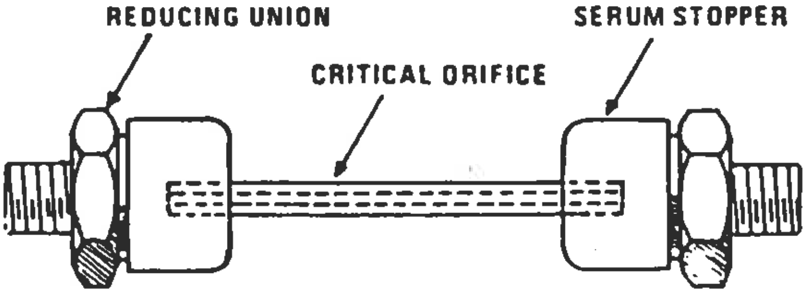

Figure 6-3. Critical orifice adaptation for Method 6 sampling train.

7.2.2 Selection of Critical Orifices. The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, i.e., a critical vacuum can be obtained, as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown below give the following approximate flow rates.

Guage/cm	Flow rate, cc/min	Gauge/cm	Flow rate, cc/min
21/7.6	1100	23/3.8	500
22/2.9	1000	23/5.1	450
22/3.8	900	24/3.2	400

Determine the suitability and the appropriate operating vaccum of the critical orifice as follows: If applicable, temporarily attach a rotameter and surge tank to the outlet of the sampling train. Turn on the pump, and adjust the valve to give a outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable reading is obtained on the rotameter. Record the critical vacuum, which is the outlet vacuum when the rotameter first reaches a stable value. Orifices that do not reach a critical value shall not be used.

7.2.3 Field Procedure.

7.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but is optional. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0–40 cc/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 254 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate not in excess of 2 percent of the average sampling rate ($\overline{Q}_{std}$) is acceptable. Carefully release the probe inlet plug before turning off the pump.

7.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative-humidity meter.

7.2.3.3 Critical Orifice Calibration. Prior to testing, at the sampling location, calibrate the entire sampling train using a 500-cc soap bubble meter which is attached to the inlet of the probe and an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6–4.

Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate, using the equations below:

$$V_{sb(std)} = V_{sb}\left(\frac{T_{std}}{T_{amb}}\right)\left(\frac{P_{bar}}{P_{std}}\right) \qquad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \qquad \text{Eq. 6-5}$$

where:

P_{bar} = Barometric pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} = Volumetric flow rate through critical orifice, scm/min (scf/min).

T_{amb} = Ambient absolute temperature of air, °K (°R).

T_{std} = Standard absolute temperature, 273°K (528°R).

V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft^3).

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).

Θ = Time, min.

Date ______________________ Train ID ______________________

Critical orifice size ______________________ Critical vacuum ______________

		Pretest	Post-test
Soap bubble meter volume, V_{sb}	cc		
	m^3 (ft^3)		
Time, θ	sec		
	min		
Barometric pressure, P_{bar}	mm Hg (in. Hg)		
Ambient temperature, t_{amb}	°C (°F)		
Inlet vacuum, P_c	mm Hg (in. Hg)		
Outlet vacuum	mm Hg (in. Hg)		
$V_{sb(std)}$	m^3 (ft^3)		
Flow rate, Q_{std}	$\frac{m^3}{min}$ $\left(\frac{ft^3}{min}\right)$		

Figure 6-4. Critical orifice calibration data.

7.2.3.4 Sampling. Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

Conduct a post-test calibration run using the calibration procedure outlined in Section 7.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 pecent, void the test run; if not, calculate the volume of the gas measured with the critical orifice, $V_{m(std)}$, using Equation 6-6 and the average of Q_{std} of both runs, as follows:

$$V_{m(std)} = \bar{Q}_{std}\, \theta_s\, (1-B_{wa}) \left(\frac{P_{bar} + P_{sr}}{P_{bar} + P_c}\right) \qquad \text{Eq. 6-6}$$

where:

$V_{m(std)}$ = Dry gas volume measured with the critical orifice, corrected to standard conditions, dscm (dscf).

$\bar{Q}_{std}$ = Average flow rate of pretest and post-test calibration runs, scm/min (scf/min).

B_{wa} = Water vapor in ambient air, proportion by volume.

θ_s = Sampling time, min.

P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

P_{sr} = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

If the percent difference between the molecular weight of the ambient air at staturated conditions and the sample gas is more than ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$V_{m(std)} = \bar{Q}_{std}\, \theta_s\, (1-B_{wa}) \sqrt{\frac{M_a}{M_s}} \left(\frac{P_{bar} + P_{sr}}{P_{bar} + P_c}\right) \qquad \text{Eq. 6-7}$$

where:

M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

Note.—A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

Drain the ice bath, and purge the sampling train using the procedure described in Section 4.1.3.

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METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x (as NO_2) per dry standard cubic meter, without having to dilute the sample.

2. *Apparatus*

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring sample volume to within ±2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within ±5 percent, will be considered acceptable alternatives, subject to approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon[1] tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

2.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1° C (2° F) intervals from −5 to 50° C (25 to 125° F).

2.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Vacuum Gauge. U-tube manometer, 1 meter (36 in.), with 1-mm (0.1-in.) divisions, or other gauge capable of measuring pressure to within ±2.5 mm Hg (0.10 in. Hg).

2.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

2.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase, or vice versa for elevation decrease.

2.2 Sample Recovery. The following equipment is required for sample recovery:

2.2.1 Graduated Cylinder. 50 ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

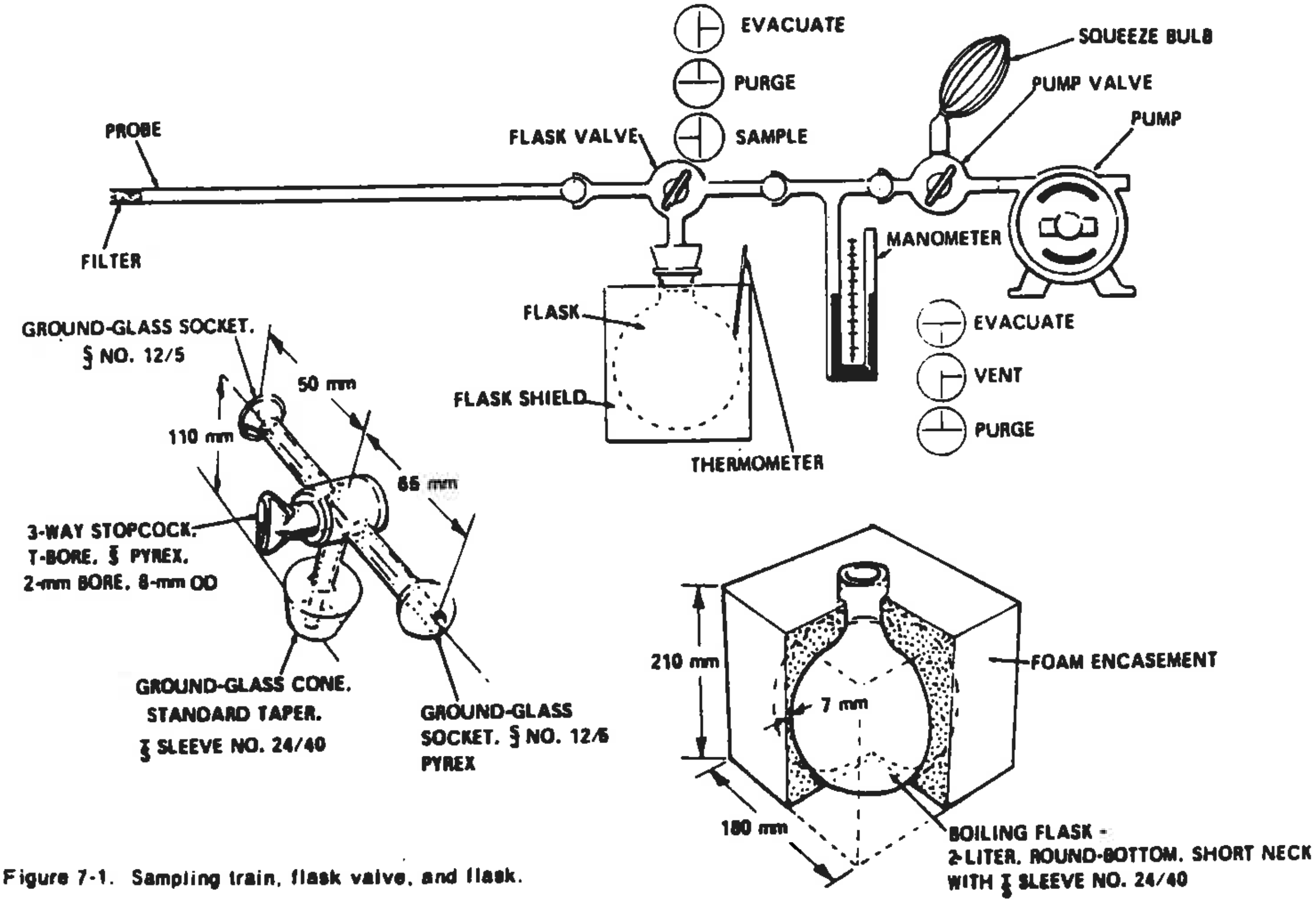

Figure 7-1. Sampling train, flask valve, and flask.

2.3 Analysis. For the analysis, the following equipment is needed:

2.3.1 Volumetric Pipettes. Two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml for each sample and standard.

2.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallow-form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70° C (160° F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper. Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

2.3.6 Graduated Cylinder. 100 ml with 1-ml divisions.

2.3.7 Volumetric Flasks. 50 ml (one for each sample and each standard), 100 ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000 ml (one).

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

2.3.9 Graduated Pipette. 10 ml with 0.1-ml divisions.

2.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3.11 Analytical Balance. To measure to within 0.1 mg.

3. *Reagents*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Two reagents are required for sample recovery:

3.2.1 Sodium Hydroxide (1*N*). Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

3.2.2 Water. Deionized, distilled to conform to ASTM specification D1193-77, Type 3 (incorporated by reference—see § 60.17). At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

3.3.2 Phenol. White solid.

3.3.3 Sulfuric Acid. Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

3.3.4 Potassium Nitrate. Dried at 105 to 110° C (220 to 230° F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.5 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1,000-ml volumetric flask.

3.3.6 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with deionized distilled water. One milliliter of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

3.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100° C (212° F) for 2 hours. Store in a dark, stoppered bottle.

3.3.9 Quality Assurance Audit Samples. Nitrate samples in glass vials prepared by EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. Each set will consist of two vials having solutions of unknown concentrations. Only when making compliance determinations, obtain an audit sample set from the quality assurance management office at each EPA regional office or the responsible enforcement agency. (NOTE: The tester should notify the quality assurance office or the responsible enforecement agency at least 30 days prior to the test date to allow sufficient time for sample delivery.)

4. *Procedures*

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been properly greased with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn the off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2), then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample Recovery. Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis. Note the level of the liquid in container and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately prior to analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the procelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled water. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds A_4, the absorbance of the 400 μg NO_2 standard (see Section 5.2.2).

4.4 Audit Sample Analysis. Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) in the same manner to evaluate the technique of the analyst and the standards preparation. (NOTE: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is the Source Branch listed in Section 3.3.9.) The same analysts, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions. (NOTE: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total μg NO_2/sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual audit concentrations. If the 10-percent specification is not met, reanalyze the compliance samples and audit samples and include initial and reanalysis values in the test report (see NOTE in the first paragraph of this section).

Failure to meet the 10-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

5. *Calibration*

5.1 Flask Volume. The volume of the collection flask-flask valve combination must be known prior to sampling. Assemble the flask and flask valve and fill with water, to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination. Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the specrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_2 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 25 to 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 4.3 until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 100 \; \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

Equation 16-1

where:

K_c = Calibration factor, μg

A_1 = Absorbance of the 100-μg NO_2 standard

A_2 = Absorbance of the 200-μg NO_2 standard

A_3 = Absorbance of the 300-μg NO_2 standard

A_4 = Absorbance of the 400-μg NO_2 standard

5.2.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K_c factor (least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. These calculated concentration values should not differ from the actual concentrations (i.e., 100, 200, 300, and 400 μg NO_2) by more than 7 percent for three of the four standards.

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6. *Calculations*

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Nomenclature.

A = Absorbance of sample.

C = Concentration of NO_x as NO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of NO_x as NO_2 in gas sample, μg.

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature 293° K (528° R)

V_{sc} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing soluton, 25 ml.

2 = 50/25, the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted).

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{sc} = \frac{T_{std}}{P_{std}} (V_f - V_a) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

$$= K_1 (V_f - 25 \text{ ml}) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Equation 7-2

$$K_1 = 0.3858 \ \frac{°K}{\text{mm Hg}} \text{ for metric units}$$

$$= 17.64 \ \frac{°R}{\text{in. Hg}} \text{ for English units}$$

6.3 Total µg NO_2 Per Sample.

$$m = 2\, K_c\, AF$$

Equation 7-3

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

6.4 Sample concentration, dry basis, corrected to standard conditions.

$$C = K_2 \frac{m}{V_{sc}}$$

Equation 7-4

6.5 Relative Error (RE) for QA Audit Samples, Percent.

$$RE = \frac{C_d - C_a}{C_a \times 100} \quad \text{Eq. } 7-5$$

Where:

C_d = Determined audit sample concentration, mg/dscm.

C_a = Actual audit sample concentration, mg/dscm.

$K_2 = 10^3$ (mg/scm)/(µg/ml) for metric units.

$= 6.242 \times 10^{-5}$ (lb/scf)/(µg/ml) for English units.

To convert from mg/dscm to g/dscm, divide C by 1.000.

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METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES—ION CHROMATOGRAPHIC METHOD

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the measurement of nitrogen oxides emitted from stationary sources; it may be used as an alternative to Method 7 (as defined in 40 CFR Part 60.8(b)) to determine compliance if the stack concentration is within the analytical range. The analytical range of the method is from 125 to 1,250 mg NO_x/m^3 as NO_2 (65 to 655 ppm), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m³ (10 ppm), but may vary among instruments.

1.2 Principle. A grab sample is collected in an evacuated flask containing a diluted sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, except nitrous oxide, are oxidized to nitrate and measured by ion chromatography.

2. *Apparatus.*

2.1 Sampling. Same as in Method 7, Section 2.1.

2.2 Sampling Recovery. Same as in Method 7, Section 2.2, except the stirring rod and pH paper are not needed.

2.3 Analysis. For the analysis, the following equipment is needed. Alternative instrumentation and procedures will be allowed provided the calibration precision in Section 5.2 and acceptable audit accuracy can be met.

2.3.1 Volumetric Pipets. Class A; 1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

2.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

2.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

2.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

2.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

2.3.4.4 Conductivity Detector.

2.3.4.5 Recorder. Compatible with the output voltage range of the detector.

3. *Reagents.*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. An absorbing solution consisting of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) is required for sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to a 1-liter flask containing water (same as § 3.2). Add 6 ml of 3 percent H_2O_2 that has been freshly prepared from 30 percent solution. Dilute to volume with water, and mix well. This absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

Note: Biased testing results have been observed when sampling under conditions of high sulfur dioxide concentrations (above 2000 ppm).

3.2 Sample Recovery. Deionized distilled water that conforms to American Society for Testing and Materials specification D 1193-74, Type 3, is required for sample recovery. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Water. Same as in Section 3.2.

3.3.2 Stock Standard Solution, 1 mg NO_3/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110°C for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

3.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

3.3.4 Eluent Solution. Weight 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$ Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

3.35 Quality Assurance Audit Samples. Same as required in Method 7.

4. *Procedure.*

4.1 Sampling. Same as in Method 7, Section 4.1.

4.2 Sample. Recovery. Same as in Method 7, Section 4.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and recovery

4.3 Sample. Preparation. Note the level of the liquid in the container and confirm whether any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used in all sample, standard, and blank dilutions.)

4.4 Analysis. Prepare a standard calibration curve according to Section 5.2. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the anlaysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

4.5 Audit Sample. Analysis. Same as required in Method 7.

5. *Calibration.*

5.1 Flask Volume. Same as in Method 7, Section 5.1.

5.2 Standard Calibration Curve. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to volume with water, and mix well. Analyze with the samples as described in Section 4.4 and subtract the blank from each value. Prepare or calculate a linear regression plot to the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (i.e., 25, 50, 100, 150, and 250 μg).

5.3 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

5.6 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in Section 2.1.6 of Method 7.

5.7 Analytical Balance. Calibrate against standard weights.

6. *Calculations.*

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

6.1 Sample Volume. Calculate the sample volume V_{sc} (in ml) on a dry basis, corrected to standard conditions, using Equation 7-2 of Method 7.

6.2 Sample Concentration of NO_x as NO_2. Calculate the sample concentration C (in mg/dscm) as follows:

$$C = \frac{HSF \times 10^4}{V_{sc}} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm

S = Calibration factor, µg/mm

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration)

10^4 = 1:10 dilution times conversion factor of

$$\frac{mg}{10^3\ \mu g} \times \frac{10^6\ ml}{m^3}$$

To convert from mg/dscm to g/dscm, divide C by 1000.

If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$ppm\ NO_2 = 0.5228\ C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

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METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the detemination of sulfuric acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter ($0.03 > 10^{-7}$ pounds/cubic foot) for sulfur trioxide and 1.2 mg/m^3 ($0.74\ 10^{-7}$ lb/ft^3) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,500 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents are present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, U. S. E. P.A., are requred.

Filterable particulate matter may be determined along with SO_2 and SO_3 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopronanol impinger (see Section 2.1 of method 6.) If this option is chosen, particulate analysis is gravimetric only; H_2SO_4 acid mist is not determined separately.

2. *Apparatus*

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 8-1; it is similiar to the Method 5 train except that the filter position is different and the filter holder does not have to be heated. Commercial models of this train are avaiable. For those who desire to build their own, however, complete construction details are described in APTD-0581. Changes from the APTD-0581 document and allowable modifications to Figure 8-1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe Nozzle. Same as Method 5, Section 2.1.1.

2.1.2 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

2.1.3 Pitot Tube. Same as Method 5, Section 2.1.3.

2.1.4 Differential Pressure Gauge. Same as Method 5, Section 2.1.4.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials, e.g., Teflon or Viton, may be used subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Note: Do not heat the filter holder.

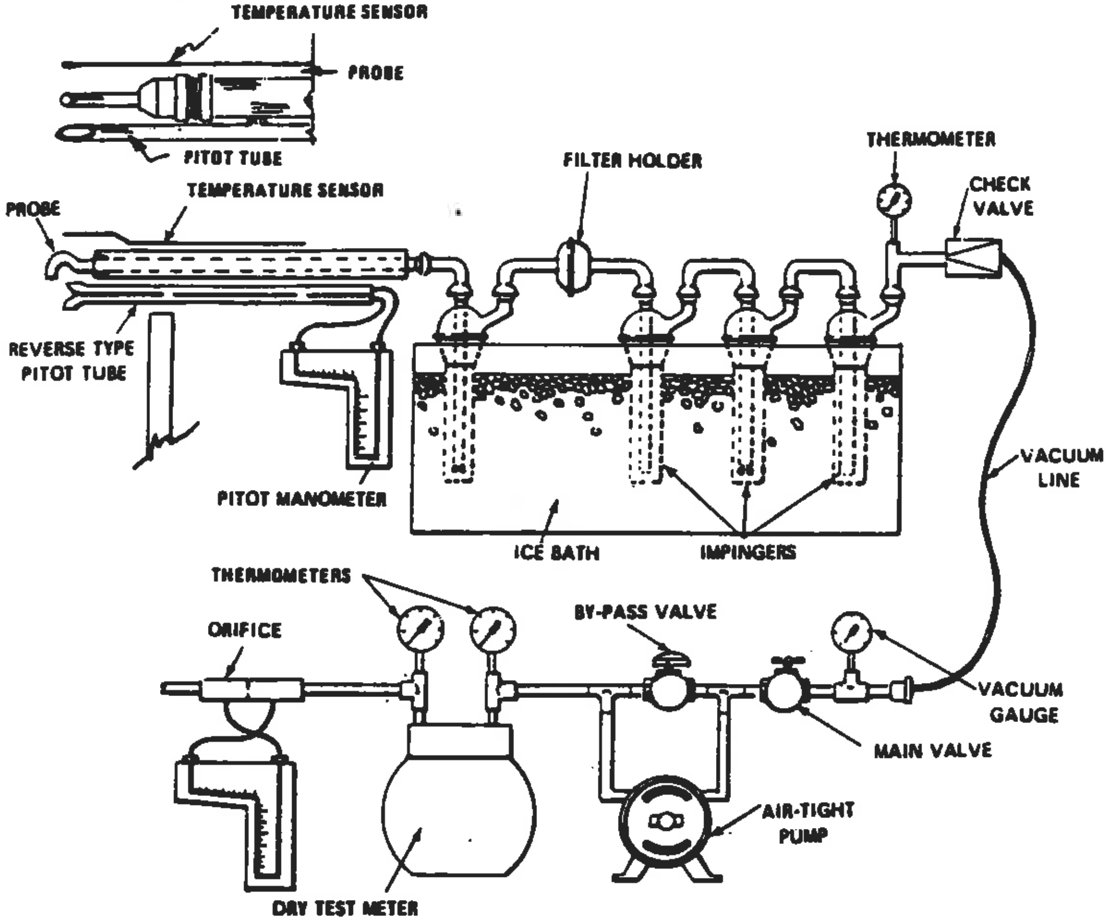

Figure 8-1. Sulfuric acid mist sampling train.

2.1.6 Impingers—Four, as shown in Figure 8-1. The first and third shall be of the Greenburg-Smith design with standard tips. The second and fourth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in.) ID glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.7 Metering System. Same as Method 5, Section 2.1.8.

2.1.8 Barometer. Same as Method 5, Section 2.1.9.

2.1.9 Gas Density Determination Equipment. Same as Method 5, Section 2.1.10.

2.1.10 Temperature Gauge. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1° C (2° F).

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500 ml. (two).

2.2.2 Graduated Cylinders. 250 ml, 1 liter. Volumetric flasks may also be used.

2.2.3 Storage Bottles. Leak-free polyethylene bottles, 1000 ml size (two for each sampling run).

2.2.4 Trip Balance. 500-gram capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

2.3 Analysis.

2.3.1 Pipettes. Volumetric 25 ml, 100 ml.

2.3.2 Burette. 50 ml.

2.3.3 Erlenmeyer Flask. 250 ml. (one for each sample blank and standard).

2.3.4. Graduated Cylinder. 100 ml.

2.3.5 Trip Balance. 500 g capacity, to measure to ±0.5g.

2.3.6 Dropping Bottle. To add indicator solution, 125-ml size.

3. *Reagents*

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

3.1 Sampling.

3.1.1 Filters. Same as Method 5, Section 3.1.1.

3.1.2 Silica Gel. Same as Method 5, Section 3.1.2.

3.1.3 Water. Deionized, distilled to conform to ASTM specification D1193-77, Type 3 (incorporated by reference—see § 60.17). At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.4 Isopropanol, 80 Percent. Mix 800 ml of isopropanol with 200 ml of deionized, distilled water.

NOTE: Experience has shown that only A.C.S. grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commerical sources occasionally has peroxide impurities that will cause erroneously high sulfuric acid mist measurement. Use the following test for detecting peroxides in each lot of isopropanol: Shake 10 ml of the isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance on a spectrophotometer at 352 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. Peroxides may be removed from isopropanol by redistilling, or by passage through a column of activated alumina. However, reagent-grade isopropanol with suitably low peroxide levels is readily available from commercial sources; therefore, rejection of contaminated lots may be more efficient than following the peroxide removal procedure.

3.1.5 Hydrogen Peroxide, 3 Percent. Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water. Prepare fresh daily.

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water. Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

3.3 Analysis.

3.3.1 Water. Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

3.3.3 Thorin Indicator. 1-(o-arsonophenylazo) 2-naphthol-3, 6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium Perchlorate (0.0100 Normal). Dissolve 1.95 g of barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$) in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol; 1.22 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

3.3.5 Sulfuric Acid Standard (0.0100 N). Purchase or standardize to ±0.0002 N against 0.0100 N NaOH that has previously been standardized against primary standard potassium acid phthalate.

3.3.6 Quality Assurance Audit Samples. Same as in Method 6, Section 3.3.6.

4. *Procedure*

FIGURE 8-2—FIELD DATA

Plant ....
Location ....
Operator ....
Date ....
Run No ....
Sample box No ....
Meter box No. ....
Meter ΔH@ ....
C factor ....
Pitot tube coefficient, Cp ....

SCHEMATIC OF STACK CROSS SECTION

Static pressure, mm Hg (in. Hg) ....
Ambient temperature ....
Barometer pressure ....
Assumed moisture, % ....
Probe length, m (ft) ....
Nozzle identification No ....
Average calibrated nozzle diameter, cm (in.) ....
Probed heater setting ....
Leak rate, m³/min, (cfm) ....
Probe liner material ....
Filter No. ....

Traverse point number	Sampling time	Vacuum	Stack temperature (T_s)	Velocity head (ΔP)	Pressure differential across orifice meter	Gas sample volume	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger
							Inlet	Outlet	
	(θ), min.	mm Hg (in. Hg)	°C (°F)	mm H_2O (in H_2O)	mm H_2O (in H_2O)	m^3 (ft^3)	°C (°F)	°C (°F)	°C (°F)
Total Average							Avg Avg	Avg	

4.1 Sampling.

4.1.1 Pretest Preparation. Follow the procedure outlined in Method 5, Section 4.1.1; filters should be inspected, but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry, i.e., moisture free, the silica gel need not be weighed.

4.1.2 Preliminary Determinations. Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of Collection Train. Follow the procedure outlined in Method 5, Section 4.1.3 (except for the second paragraph and other obviously inapplicable parts) and use Figure 8-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide in both the second and third impingers; retain a portion of each reagent for used as a blank solution. Place about 200g of silica gel in the fourth impinger.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g and record these weights. The weight of the silica gel (or silica gel plus container) must also be determined to the nearest 0.5 g and recorded.

4.1.4 Pretest Leak-Check Procedure. Follow the basic procedure outlined in Method 5, Section 4.1.4.1, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as, ". . . plugging the inlet to the filter holder . . .," shall be replaced by, ". . . plugging the inlet to the first impinger . . ." The pretest leak-check is optional.

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as in Section 4.1.4.3 of Method 5 (with appropriate modification) and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, the tester shall either correct the sample volume, as outlined in Section 6.3 of Method 5, or shall void the run.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train, by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. At the option of the tester, ambient air (without cleaning) may be used.

4.1.6 Calculation of Percent Isokinetic. Follow the procedure outlined in Method 5, Section 4.1.6.

4.2 Sample Recovery.

4.2.1 Container No. 1. If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g and record this weight.

Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on the container and identify the sample container.

4.2.2 Container No. 2. If a moisture content analysis is to be done, weigh the second and third impingers (plus contents) to the nearest 0.5 g and record these weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with deionized, distilled water, and add this rinse water to the cylinder. Dilute to a volume of 1000 ml with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on the container. Seal and identify the sample container.

4.3 Analysis.

Note the level of liquid in containers 1 and 2, and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occured, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

4.3.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for and few minutes before removing a sample. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

4.4 Quality Control Procedures. Same as in Method 5, Section 4.4.

4.5 Audit Sample Analysis. Same as in Method 6, Section 4.4.

5. *Calibration.*

5.1 Calibrate equipment using the procedures specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); Section 5.7 (barometer). Note that the recommended leak-check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2 Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of 100 percent isopropanol has been added.

6. *Calculations*

NOTE: Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A_n=Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws}=Water vapor in the gas stream, proportion by volume.

$C_{H_2SO_4}$=Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2}=Sulfur dioxide concentration, g/dscm (lb/dscf).

I=Percent of isokinetic sampling.

N=Normality of barium perchlorate titrant, 'meq/ml".

P_{bar}=Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s=Absolute stack gas pressure, mm Hg (in. Hg).

P_{std}=Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m=Average absolute dry gas meter temperature (see Figure 8-2), ° K (° R).

T_s=Average absolute stack gas temperature (see Figure 8-2), ° K (° R).

T_{std}=Standard absolute temperature, 293° K (528° R).

V_a=Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{lc}=Total volume of liquid collected in impingers and silica gel, ml.

V_m=Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$=Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

v_s=Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from method 8, m/sec (ft/sec).

V_{soln}=Total volume of solution in which the sufuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.

V_t=Volume of barium perchlorate titrant used for the sample, ml.

V_{tb}=Volume of barium perchlorate titrant used for the blank, ml.

Y=Dry gas meter calibration factor.

ΔH=Average pressure drop across orifice meter, mm (in.) H_2O.

θ=Total sampling time, min.

13.6=Specific gravity of mercury.

60=sec/min.

100=Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 8-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C and 760 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation 8-1

where:

K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in.. Hg for English units.

NOTE: If the leak rate observed during any mandatory leak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_m in Equation 8-1 (as described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor using Equation 5-2 of Method 5; the weight of water collected in the impingers and silica gel can be directly converted to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas, using Equation 5-3 of Method 5. The "Note" in Section 6.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

$$C_{H_2SO_4} = K_2 \frac{N(V_t - V_{tb})\left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 8-2

where:

K_2 = 0.04904 g/milliequivalent for metric units.

= 1.081×10^{-4} lb/meq for English units.

6.6 Sulfur dioxide concentration.

$$C_{SO_2} = K_3 \frac{N(V_t - V_{tb})\left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 8-3

where:

K_3 = 0.03203 g/meq for metric units.

= 7.061×10^{-5} lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$V_mY$$

$$I = \frac{100T_s[K_4V_{lc}+(\uparrow/T_m)P_{bar}+\Delta H/13.6)]}{60\theta V_sP_sA_n}$$

Equation 8-4

where:

K_4 = 0.003464 mm Hg-m³/ml-°K for metric units.

= 0.002676 in. Hg-ft³/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60 (1 - B_{ws})}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Equation 8-5

where:

K_5 = 4.320 for metric units.

= 0.09450 for English units

6.8 Acceptable Results. If 90 percent < I < 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may opt to accept the results. Use Citation 4 in the Bibliography of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

6.9 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 5.2 and 5.3 of Method 2.

6.10 Relative Error (RE) for QA Audit Samples. Same as in Method 6, Section 4.4.

7. *Bibliography*

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7. Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. pp. 40-42. American Society for Testing and Materials. Philadelphia, Pa. 1974.

METHOD 9—VISUAL DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES

Many stationary sources discharge visible emissions into the atmosphere; these emissions are usually in the shape of a plume. This method involves the determination of plume opacity by qualified observers. The method includes procedures for the training and certification of observers, and procedures to be used in the field for determination of plume opacity. The appearance of a plume as viewed by an observer depends upon a number of variables, some of which may be controllable and some of which may not be controllable in the field. Variables which can be controlled to an extent to which they no longer exert a significant influence upon plume appearance include: Angle of the observer with respect to the plume; angle of the observer with respect to the sun; point of observation of attached and detached steam plume; and angle of the observer with respect to a plume emitted from a rectangular stack with a large length to width ratio. The method includes specific criteria applicable to these variables.

Other variables which may not be controllable in the field are luminescence and color contrast between the plume and the background against which the plume is viewed. These variables exert an influence upon the appearance of a plume as viewed by an observer, and can affect the ability of the observer to accurately assign opacity values to the observed plume. Studies of the theory of plume opacity and field studies have demonstrated that a plume is most visible and presents the greatest apparent opacity when viewed against a contrasting background. It follows from this, and is confirmed by field trials, that the opacity of a plume, viewed under conditions where a contrasting background is present can be assigned with the greatest degree of accuracy. However, the potential for a positive error is also the greatest when a plume is viewed under such contrasting conditions. Under conditions presenting a less contrasting background, the apparent opacity of a plume is less and approaches zero as the color and luminescence contrast decrease toward zero. As a result, significant negative bias and negative errors can be made when a plume is viewed under less contrasting conditions. A negative bias decreases rather than increases the possibility that a plant operator will be cited for a violation of opacity standards due to observer error.

Studies have been undertaken to determine the magnitude of positive errors which can be made by qualified observers while reading plumes under contrasting conditions and using the procedures set forth in this method. The results of these studies (field trials) which involve a total of 769 sets of 25 readings each are as follows:

(1) For black plumes (133 sets at a smoke generator), 100 percent of the sets were read with a positive error[1] of less than 7.5 percent opacity; 99 percent were read with a positive error of less than 5 percent opacity.

(2) For white plumes (170 sets at a smoke generator, 168 sets at a coal-fired power plant, 298 sets at a sulfuric acid plant), 99 percent of the sets were read with a positive error of less than 7.5 percent opacity; 95 percent were read with a positive error of less than 5 percent opacity.

The positive observational error associated with an average of twenty-five readings is therefore established. The accuracy of the method must be taken into account when determining possible violations of applicable opacity standards.

1. *Principle and applicability.*

1.1 Principle. The opacity of emissions from stationary sources is determined visually by a qualified observer.

1.2 Applicability. This method is applicable for the determination of the opacity of emissions from stationary sources pursuant to § 60.11(b) and for qualifying observers for visually determining opacity of emissions.

2. *Procedures.* The observer qualified in accordance with paragraph 3 of this method shall use the following procedures for visually determining the opacity of emissions:

2.1 Position. The qualified observer shall stand at a distance sufficient to provide a clear view of the emissions with the sun oriented in the 140° sector to his back. Consistent with maintaining the above requirement, the observer shall, as much as possible, make his observations from a position such that his line of vision is approximately perpendicular to the plume direction, and when observing opacity of emissions from rectangular outlets (e.g. roof monitors, open baghouses, noncircular stacks), approximately perpendicular to the longer axis of the outlet. The observer's line of sight should not include more than one plume at a time when multiple stacks are involved, and in any case the observer should make his observations with his line of sight perpendicular to the longer axis of such a set of multiple stacks (e.g. stub stacks on baghouses).

2.2 Field records. The observer shall record the name of the plant, emission location, type facility, observer's name and affiliation* and the date on a field data sheet (Figure 9-1). The time, estimated distance to the emission location, approximate wind direction, estimated wind speed, description of the sky condition (presence and color of clouds), and plume background are recorded on a field data sheet at the time opacity readings are initiated and completed.

2.3 Observations. Opacity observations shall be made at the point of greatest opacity in that portion of the plume where condensed water vapor is not present. The observer shall not look continuously at the plume, but instead shall observe the plume momentarily at 15-second intervals.

2.3.1 Attached steam plumes. When condensed water vapor is present within the plume as it emerges from the emission outlet, opacity observations shall be made beyond the point in the plume at which condensed water vapor is no longer visible. The observer shall record the approximate distance from the emission outlet to the point in the plume at which the observations are made.

2.3.2 Detached steam plume. When water vapor in the plume condenses and becomes visible at a distinct distance from the emission outlet, the opacity of emissions should be evaluated at the emission outlet prior to the condensation of water vapor and the formation of the steam plume.

2.3.3 Fugitive emissions. The guidelines for positioning of the observer in relation to the stack found in paragraph 2.1 can be applied to determination of visible opacity from fugitive emission sources. That is, the observer should have a clear view of the source and the potential emissions with the sun or other light source at his back. A position at least 15 feet from the source, but permitting a clear, unobstructed view of the source, is recommended. To the extent feasible, the line of sight should be approximately perpendicular to the flow of potential fugitive emissions, and, also, to the longer axis to the potential fugitive emissions. Readings of opacity should be made for the point(s) of highest opacity within the visible fugitive emission. The highest opacity usually occurs immediately above or immediately downwind of the source, so observers should concentrate on the area(s) close to the source.

2.4 Recording observations. Opacity observations shall be recorded to the nearest 5 percent at 15-second intervals on an observational record sheet. (See Figure 9-2 for an example.) A minimum of 24 observations shall be recorded. Each momentary observation recorded shall be deemed to represent the average opacity of emissions for a 15-second period.

2.5 Data Reduction. Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. Divide the observations recorded on the record sheet into sets of 24 consecutive observations. A set is composed of any 24 consecutive observations. Sets need not be consecutive in time and in no case shall two sets overlap. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum

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[1] For a set, positive error = average opacity determined by observers' 25 observations—average opacity determined from transmissometer's 25 recordings.

* Section 2.2. by adding the words "a sketch of the observer's position relative to the source." between the words "affiliation," and "and" to read ". . . affiliation, a sketch of the observer's position relative to the source, and . . ."

by 24. If an applicable standard specifies an averaging time requiring more than 24 observations, calculate the average for all observations made during the specified time period. Record the average opacity on a record sheet. (See Figure 9-1 for an example.)

3. *Qualifications and testing.*

3.1 Certification requirements. To receive certification as a qualified observer, a candidate must be tested and demonstrate the ability to assign opacity readings in 5 percent increments to 25 different black plumes and 25 different white plumes, with an error not to exceed 15 percent opacity on any one reading and an average error not to exceed 7.5 percent opacity in each category. Candidates shall be tested according to the procedures described in paragraph 3.2. Smoke generators used pursuant to paragraph 3.2 shall be equipped with a smoke meter which meets the requirements of paragraph 3.3.

The certification shall be valid for a period of 6 months, at which time the qualification procedure must be repeated by any observer in order to retain certification.

3.2 Certification procedure. The certification test consists of showing the candidate a complete run of 50 plumes—25 black plumes and 25 white plumes—generated by a smoke generator. Plumes within each set of 25 black and 25 white runs shall be presented in random order. The candidate assigns an opacity value to each plume and records his observation on a suitable form. At the completion of each run of 50 readings, the score of the candidate is determined. If a candidate fails to qualify, the complete run of 50 readings must be repeated in any retest. The smoke test may be administered as part of a smoke school or training program, and may be preceded by training or familiarization runs of the smoke generator during which candidates are shown black and white plumes of known opacity.

3.3 Smoke generator specifications. Any smoke generator used for the purposes of paragraph 3.2 shall be equipped with a smoke meter installed to measure opacity across the diameter of the smoke generator stack. The smoke meter output shall display instack opacity based upon a pathlength equal to the stack exit diameter, on a full 0 to 100 percent chart recorder scale. The smoke meter optical design and performance shall meet the specifications shown in Table 9-1. The smoke meter shall be calibrated as prescribed in paragraph 3.3.1 prior to the conduct of each smoke reading test. At the completion of each test, the zero and span drift shall be checked and if the drift exceeds ±1 percent opacity, the condition shall be corrected prior to conducting any subsequent test runs. The smoke meter shall be demonstrated, at the time of installation, to meet the specifications listed in Table 9-1. This demonstration shall be repeated following any subsequent repair or replacement of the photocell or associated electronic circuitry including the chart recorder or output meter, or every 6 months, whichever occurs first.

TABLE 9-1—SMOKE METER DESIGN AND PERFORMANCE SPECIFICATIONS

Parameter	Specification
a. Light source	Incandescent lamp operated at nominal rated voltage.
b. Spectral response of photocell.	Photopic (daylight spectral response of the human eye—reference 4.3).
c. Angle of view	15° maximum total angle.
d. Angle of projection	15° maximum total angle.
e. Calibration error	±3% opacity, maximum.
f. Zero and span drift±1% opacity, 30 minutes.	
g. Response time	5 seconds.

3.3.1 Calibration. The smoke meter is calibrated after allowing a minimum of 30 minutes warmup by alternately producing simulated opacity of 0 percent and 100 percent. When stable response at 0 percent or 100 percent is noted, the smoke meter is adjusted to produce an output of 0 percent or 100 percent, as appropriate. This calibration shall be repeated until stable 0 percent and 100 percent readings are produced without adjustment. Simulated 0 percent and 100 percent opacity values may be produced by alternately switching the power to the light source on and off while the smoke generator is not producing smoke.

3.3.2 Smoke meter evaluation. The smoke meter design and performance are to be evaluated as follows:

3.3.2.1 Light source. Verify from manufacturer's data and from voltage measurements made at the lamp, as installed, that the lamp is operated within ±5 percent of the nominal rated voltage.

3.3.2.2 Spectral response of photocell. Verify from manufacturer's data that the photocell has a photopic response; i.e., the spectral sensitivity of the cell shall closely approximate the standard spectral-luminosity curve for photopic vision which is referenced in (b) of Table 9-1.

FIGURE 9-1
RECORD OF VISUAL DETERMINATION OF OPACITY

PAGE____of____

COMPANY____________________
LOCATION____________________
TEST NUMBER____________________
DATE____________________
TYPE FACILITY____________________
CONTROL DEVICE____________________

HOURS OF OBSERVATION____________________
OBSERVER____________________
OBSERVER CERTIFICATION DATE____________________
OBSERVER AFFILIATION____________________
POINT OF EMISSIONS____________________
HEIGHT OF DISCHARGE POINT____________________

CLOCK TIME	Initial			Final
OBSERVER LOCATION Distance to Discharge				
Direction from Discharge				
Height of Observation Point				
BACKGROUND DESCRIPTION				
WEATHER CONDITIONS Wind Direction				
Wind Speed				
Ambient Temperature				
SKY CONDITIONS (clear, overcast, % clouds, etc.)				
PLUME DESCRIPTION Color				
Distance Visible				
OTHER INFORMATION				

SUMMARY OF AVERAGE OPACITY

Set Number	Time	Opacity	
	Start--End	Sum	Average

Readings ranged from ____ to ____ % opacity

The source was/was not in compliance with ____ at the time evaluation was made.

FIGURE 9-2—OBSERVATION RECORD

Page ___ of ___

Company ____________________
Location ____________________
Test Number ____________________
Date ____________________

Observer ____________________
Type facility ____________________
Point of emissions ____________________

Hr	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	0							
	1							
	2							
	3							
	4							
	5							
	6							
	7							
	8							
	9							
	10							
	11							
	12							
	13							
	14							
	15							
	16							
	17							
	18							
	19							
	20							
	21							
	22							
	23							
	24							
	25							
	26							
	27							
	28							
	29							

FIGURE 9-2—OBSERVATION RECORD—(CONTINUED)

Page ___ of ___

Company ____________________
Location ____________________
Test Number ____________________
Date ____________________

Observer ____________________
Type facility ____________________
Point of emissions ____________________

Hr	Min.	Seconds				Steam plume (check if applicable)		Comments
		0	15	30	45	Attached	Detached	
	30							
	31							
	32							
	33							
	34							
	35							
	36							
	37							
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	59							

3.3.2.3 Angle of view. Check construction geometry to ensure that the total angle of view of the smoke plume, as seen by the photocell, does not exceed 15°. The total angle of view may be calculated from: $\Phi=2\tan^{-1}d/2L$, where θ=total angle of view; d=the sum of the photocell diameter+the diameter of the limiting aperture; and L=the distance from the photocell to the limiting aperture. The limiting aperture is the point in the path between the photocell and the smoke plume where the angle of view is most restricted. In smoke generator smoke meters this is normally an orifice plate.

3.3.2.4 Angle of projection. Check construction geometry to ensure that the total angle of projection of the lamp on the smoke plume does not exceed 15°. The total angle of projection may be calculated from: $\theta=2\tan^{-1}d/2L$, where θ= total angle of projection; d= the sum of the length of the lamp filament + the diameter of the limiting aperture; and L= the distance from the lamp to the limiting aperture.

3.3.2.5 Calibration error. Using neutral-density filters of known opacity, check the error between the actual response and the theoretical linear response of the smoke meter. This check is accomplished by first calibrating the smoke meter according to 3.3.1 and then inserting a series of three neutral-density filters of nominal opacity of 20, 50, and 75 percent in the smoke meter pathlength. Filters calibrated within ±2 percent shall be used. Care should be taken when inserting the filters to prevent stray light from affecting the meter. Make a total of five nonconsecutive readings for each filter. The maximum error on any one reading shall be 3 percent opacity.

3.3.2.6 Zero and span drift. Determine the zero and span drift by calibrating and operating the smoke generator in a normal manner over a 1-hour period. The drift is measured by checking the zero and span at the end of this period.

3.3.2.7 Response time. Determine the response time by producing the series of five simulated 0 percent and 100 percent opacity values and observing the time required to reach stable response. Opacity values of 0 percent and 100 percent may be simulated by alternately switching the power to the light source off and on while the smoke generator is not operating.

4. *References.*

4.1 Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.

4.2 Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, N.C., APTD-1100, August 1972, pp. 4.1-4.36.

4.3 Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., N.Y., N.Y., 1958, Table 3.1, p. 6-52.

ALTERNATE METHOD 1—DETERMINATION OF THE OPACITY OF EMISSIONS FROM STATIONARY SOURCES REMOTELY BY LIDAR

This alternate method provides the quantitative determination of the opacity of an emissions plume remotely by a mobile lidar system (laser radar; Light Detection and Ranging). The method includes procedures for the calibration of the lidar and procedures to be used in the field for the lidar determination of plume opacity. The lidar is used to measure plume opacity during either day or nighttime hours because it contains its own pulsed light source or transmitter. The operation of the lidar is not dependent upon ambient lighting conditions (light, dark, sunny or cloudy).

The lidar mechanism or technique is applicable to measuring plume opacity at numerous wavelengths of laser radiation. However, the performance evaluation and calibration test results given in support of this method apply only to a lidar that employs a ruby (red light) laser [Reference 5.1].

1. Principle and Applicability

1.1 Principle. The opacity of visible emissions from stationary sources (stacks, roof vents, etc.) is measured remotely by a mobile lidar (laser radar).

1.2 Applicability. This method is applicable for the remote measurement of the opacity of visible emissions from stationary sources during both nighttime and daylight conditions, pursuant to 40 CFR § 60.11(b). It is also applicable for the calibration and performance verification of the mobile lidar for the measurement of the opacity of emissions. A performance/design specification for a basic lidar system is also incorporated into this method.

1.3 Definitions.

Azimuth angle: The angle in the horizontal plane that designates where the laser beam is pointed. It is measured from an arbitrary fixed reference line in that plane.

Backscatter: The scattering of laser light in a direction opposite to that of the incident laser beam due to reflection from particulates along the beam's atmospheric path which may include a smoke plume.

Backscatter signal: The general term for the lidar return signal which results from laser light being backscattered by atmospheric and smoke plume particulates.

Convergence distance: The distance from the lidar to the point of overlap of the lidar receiver's field-of-view and the laser beam.

Elevation angle: The angle of inclination of the laser beam referenced to the horizontal plane.

Far region: The region of the atmosphere's path along the lidar line-of-sight beyond or behind the plume being measured.

Lidar: Acronym for Light Detection and Ranging.

Lidar range: The range or distance from the lidar to a point of interest along the lidar line-of-sight.

Near region: The region of the atmospheric path along the lidar line-of-sight between the lidar's convergence distance and the plume being measured.

Opacity: One minus the optical transmittance of a smoke plume, screen target, etc.

Pick interval: The time or range intervals in the lidar backscatter signal whose minimum average amplitude is used to calculate opacity. Two pick intervals are required, one in the near region and one in the far region.

Plume: The plume being measured by lidar.

Plume signal: The backscatter signal resulting from the laser light pulse passing through a plume.

$1/R^2$ correction: The correction made for the systematic decrease in lidar backscatter signal amplitude with range.

Reference signal: The backscatter signal resulting from the laser light pulse passing through ambient air.

Sample interval: The time period between successive samples for a digital signal or between successive measurements for an analog signal.

Signal spike: An abrupt, momentary increase and decrease in signal amplitude.

Source: The source being tested by lidar.

Time reference: The time (t_o) when the laser pulse emerges from the laser, used as the reference in all lidar time or range measurements.

2. Procedures.

The mobile lidar calibrated in accordance with Paragraph 3 of this method shall use the following procedures for remotely measuring the opacity of stationary source emissions:

2.1 Lidar Position. The lidar shall be positioned at a distance from the plume sufficient to provide an unobstructed view of the source emissions. The plume must be at a range of at least 50 meters or three consecutive pick intervals (whichever is greater) from the lidar's transmitter/receiver convergence distance along the line-of-sight. The maximum effective opacity measurement distance of the lidar is a function of local atmospheric conditions, laser beam diameter, and plume diameter. The test position of the lidar shall be selected so that the diameter of the laser beam at the measurement point within the plume shall be no larger than three-fourths the plume diameter. The beam diameter is calculated by Equation (AM1-1):

$$D(\text{lidar}) = A + R\phi < 0.75\ D(\text{Plume}) \quad (\text{AM1-1})$$

where:

D(Plume) = diameter of the plume (cm),
ϕ = laser beam divergence measured in radians
R = range from the lidar to the source (cm)
D(Lidar) = diameter of the laser beam at range R (cm),
A = diameter of the laser beam or pulse where it leaves the laser.

The lidar range, R, is obtained by aiming and firing the laser at the emissions source structure immediately below the outlet. The range value is then determined from the backscatter signal which consists of a signal spike (return from source structure) and the atmospheric backscatter signal [Reference 5.1]. This backscatter signal should be recorded.

When there is more than one source of emissions in the immediate vicinity of the plume, the lidar shall be positioned so that the laser beam passes through only a single plume, free from any interference of the other plumes for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume along the line-of-sight (determined from the backscatter signals). The lidar shall initially be positioned so that its line-of-sight is approximately perpendicular to the plume.

When measuring the opacity of emissions from rectangular outlets (e.g., roof monitors, open baghouses, noncircular stacks, etc.), the lidar shall be placed in a position so that its line-of-sight is approximately perpendicular to the longer (major) axis of the outlet.

2.2 Lidar Operational Restrictions. The lidar receiver shall not be aimed within an angle of ± 15° (cone angle) of the sun.

This method shall not be used to make opacity measurements if thunderstorms, snowstorms, hail storms, high wind, high-ambient dust levels, fog or other atmospheric conditions cause the reference signals to consistently exceed the limits specified in Section 2.3.

2.3 Reference Signal Requirements. Once placed in its proper position for opacity measurement, the laser is aimed and fired with the line-of-sight near the outlet height and rotated horizontally to a position clear of the source structure and the associated plume. The backscatter signal obtained from this position is called the ambient-air or reference signal. The lidar operator shall inspect this signal [Section V of Reference 5.1] to: (1) determine if the lidar line-of-sight is free from interference from other plumes and from physical obstructions such as cables, power lines, etc., for a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, and (2) obtain a qualitative measure of the homogeneity of the ambient air by noting any signal spikes.

Should there be any signal spikes on the reference signal within a minimum of 50 meters or three consecutive pick intervals (whichever is greater) in each region before and beyond the plume, the laser shall be fired three more times and the operator shall inspect the reference signals on the display. If the spike(s) remains, the azimuth angle shall be changed and the above procedures conducted again. If the spike(s) disappears in all three reference signals, the lidar line-of-sight is acceptable if there is shot-to-shot consistency and there is no interference from other plumes.

Shot-to-shot consistency of a series of reference signals over a period of twenty seconds is verified in either of two ways. (1) The lidar operator shall observe the reference signal amplitudes. For shot-to-shot consistency the ratio of R_f to R_n [amplitudes of the near and far region pick intervals (Section 2.6.1)] shall vary by not more than ± 6% between shots; or (2) the lidar operator shall accept any one of the reference signals and treat the other two as plume signals; then the opacity for each of the subsequent reference signals is calculated (Equation AM1-2). For shot-to-shot consistency, the opacity values shall be within ± 3% of 0% opacity and the associated S_o values less than or equal to 8% (full scale) [Section 2.6].

If a set of reference signals fails to meet the requirements of this section, then all plume signals [Section 2.4] from the last set of acceptable reference signals to the failed set shall be discarded.

2.3.1 Initial and Final Reference Signals. Three reference signals shall be obtained within a 90-second time period prior to any data run. A final set of three reference signals shall be obtained within three (3) minutes after the completion of the same data run.

2.3.2 Temporal Criterion for Additional Reference Signals. An additional set of reference signals shall be obtained during a data run if there is a change in wind direction or plume drift of 30° or more from the direction that was prevalent when the last set of reference signals was obtained. An additional set of reference signals shall also be obtained if there is an increase in value of S_n (near region standard deviation, Equation AM1-5) or S_f (far region standard deviation, Equation AM1-6) that is greater than 6% (full scale) over the respective values calculated from the immediately previous plume signal, and this increase in value remains for 30 seconds or longer. An additional set of reference signals shall also be obtained if there is a change in amplitude in either the near or the far region of the plume signal, that is greater than 6% of the near signal amplitude and this change in amplitude remains for 30 seconds or more.

2.4 Plume Signal Requirements. Once properly aimed, the lidar is placed in operation with the nominal pulse or firing rate of six pulses/minute (1 pulse/10 seconds). The lidar operator shall observe the plume backscatter signals to determine the need for additional reference signals as required by Section 2.3.2. The plume signals are recorded from lidar start to stop and are called a data run. The length of a data run is determined by operator discretion. Short-term stops of the lidar to record additional reference signals do not constitute the end of a data run if plume signals are resumed within 90 seconds after the reference signals have been recorded, and the total stop or interrupt time does not exceed 3 minutes.

2.4.1 Non-hydrated Plumes. The laser shall be aimed at the region of the plume which displays the greatest opacity. The lidar operator must visually verify that the laser is aimed clearly above the source exit structure.

2.4.2 Hydrated Plumes. The lidar will be used to measure the opacity of hydrated or so-called steam plumes. As listed in the reference method, there are two types, i.e., attached and detached steam plumes.

2.4.2.1 Attached Steam Plumes. When condensed water vapor is present within a plume, lidar opacity measurements shall be made at a point within the residual plume where the condensed water vapor is no longer visible. The laser shall be aimed into the most dense region (region of highest opacity) of the residual plume.

During daylight hours the lidar operator locates the most dense portion of the residual plume visually. During nighttime hours a high-intensity spotlight, night vision scope, or low light level TV, etc., can be used as an aid to locate the residual plume. If visual determination is ineffective, the lidar may be used to locate the most dense region of the residual plume by repeatedly measuring opacity, along the longitudinal axis or center of the plume from the emissions outlet to a point just beyond the steam plume. The lidar operator should also observe color differences and plume reflectivity to ensure that the lidar is aimed completely within the residual plume. If the operator does not obtain a clear indication of the location of the residual plume, this method shall not be used.

Once the region of highest opacity of the residual plume has been located, aiming adjustments shall be made to the laser line-of-sight to correct for the following: movement to the region of highest opacity out of the lidar line-of-sight (away from the laser beam) for more than 15 seconds, expansion of the steam plume (air temperature lowers and/or relative humidity increases) so that it just begins to encroach on the field-of-view of the lidar's optical telescope receiver, or a decrease in the size of the steam plume (air temperature higher and/or relative humidity decreases) so that regions within the residual plume whose opacity is higher than the one being monitored, are present.

2.4.2.2 Detached Steam Plumes. When the water vapor in a hydrated plume condenses and becomes visible at a finite distance from the stack or source emissions outlet, the opacity of the emissions shall be measured in the region of the plume clearly above the emissions outlet and below condensation of the water vapor.

During daylight hours the lidar operators can visually determine if the steam plume is detached from the stack outlet. During nighttime hours a high-intensity spotlight, night vision scope, low light level TV, etc., can be used as an aid in determining if the steam plume is detached. If visual determination is ineffective, the lidar may be used to determine if the steam plume is detached by repeatedly measuring plume opacity from the outlet to the steam plume along the plume's longitudinal axis or center line. The lidar operator should also observe color differences and plume reflectivity to detect a detached plume. If the operator does not obtain a clear indication of the location of the detached plume, this method shall not be used to make opacity measurements between the outlet and the detached plume.

Once the determination of a detached steam plume has been confirmed, the laser shall be aimed into the region of highest opacity in the plume between the outlet and the formation of the steam plume. Aiming adjustments shall be made to the lidar's

LIDAR LOG CONTROL NUMBER TABULATION

Log Book Number-________

(Assign a CONTROL NUMBER to each individual source under test)

CONTROL NUMBER	DATE ASSIGNED	PROJECT	CITY, STATE

continued on next page

LIDAR LOG CONTROL NUMBER TABULATION (cont')

(Assign a CONTROL NUMBER to each individual source under test)

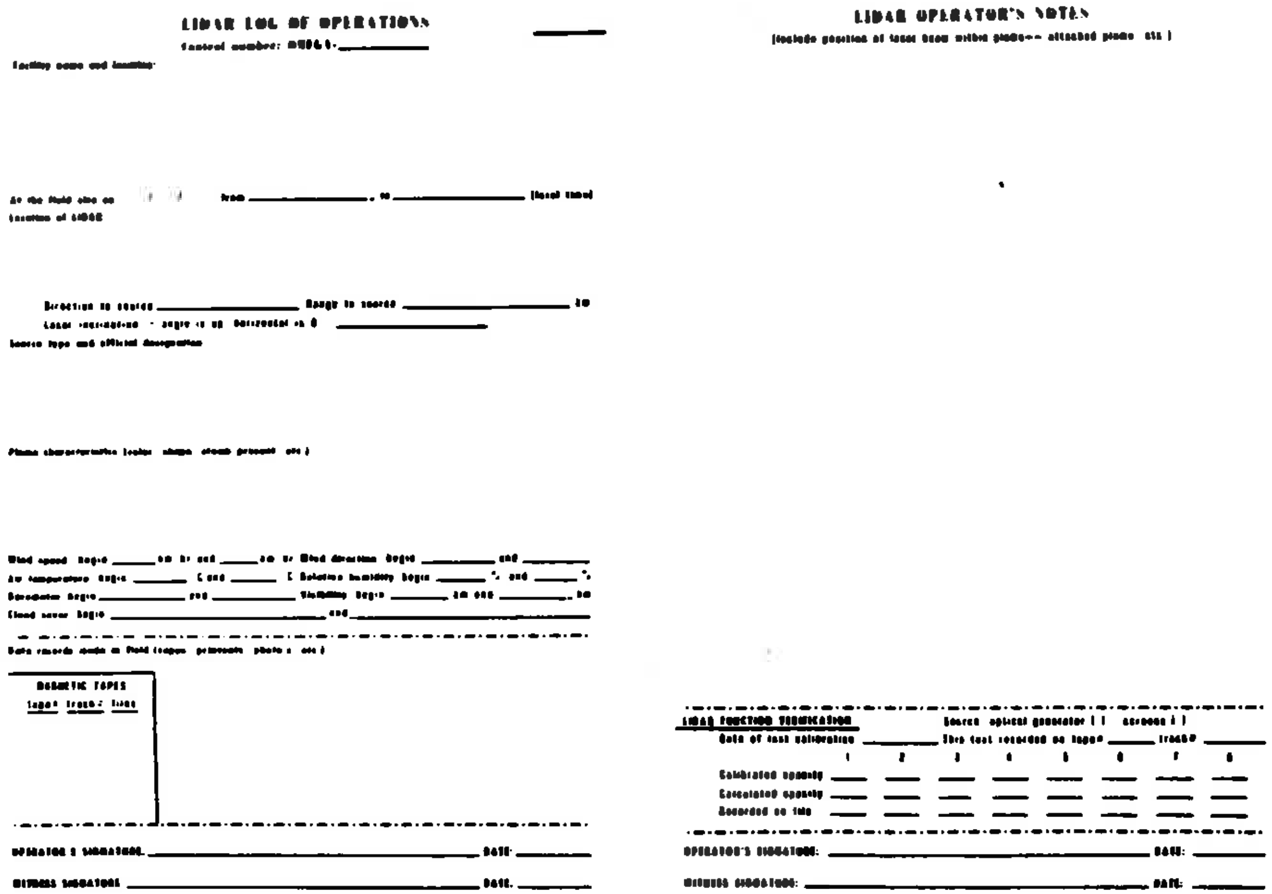
CONTROL NUMBER	DATE ASSIGNED	PROJECT	CITY, STATE

Next Log Book Number-________

Figure AM1-1 Lidar Log Control Number Tabulation line-of-sight within the plume to correct for changes in the location of the most dense region of the plume due to changes in wind direction and speed or if the detached steam plume moves closer to the source outlet encroaching on the most dense region of the plume. If the detached steam plume should move too close to the source outlet for the lidar to make interference-free opacity measurements, this method shall not be used.

2.5 Field Records. In addition to the recording recommendations listed in other sections of this method the following records should be maintained. Each plume measured should be uniquely identified. The name of the facility, type of facility, emission source type, geographic location of the lidar with respect to the plume, and plume characteristics should be recorded. The date of the test, the time period that a source was monitored, the time (to the nearest second) of each opacity measurement, and the sample interval should also be recorded. The wind speed, wind direction, air temperature, relative humidity, visibility (measured at the lidar's position), and cloud cover should be recorded at the beginning and end of each time period for a given source. A small sketch depicting the location of the laser beam within the plume should be recorded.

If a detached or attached steam plume is present at the emissions source, this fact should be recorded. Figures AM1-I and AM1-II are examples of logbook forms that may be used to record this type of data. Magnetic tape or paper tape may also be used to record data.



LIDAR LOG OF OPERATIONS

LIDAR OPERATOR'S NOTES

MAGNETIC TAPES

LIDAR FUNCTION VERIFICATION

	1	2	3	4	5	6	7	8
Calibrated opacity								
Calculated opacity								
Recorded on tape								

OPERATOR'S SIGNATURE: ____ DATE: ____

WITNESS SIGNATURE: ____ DATE: ____

Figure AM1-II Lidar Log Of Operations

2.6 Opacity Calculation and Data Analysis. Referring to the reference signal and plume signal in Figure AM1-III, the measured opacity (O_p) in percent for each lidar measurement is calculated using Equation AM1-2. ($O_p=1-T_p$; T_p is the plume transmittance.)

$$O_p = (100\%)\left[1-\left(\frac{I_f}{R_f}\,\frac{R_n}{I_n}\right)^{\frac{1}{2}}\right]$$

(AM1-2)

where:

I_n=near-region pick interval signal amplitude, plume signal, $1/R^2$ corrected.

I_f=far-region pick interval signal amplitude, plume signal, $1/R^2$ corrected.

R_n=near-region pick interval signal amplitude, reference signal, $1/R^2$ corrected, and

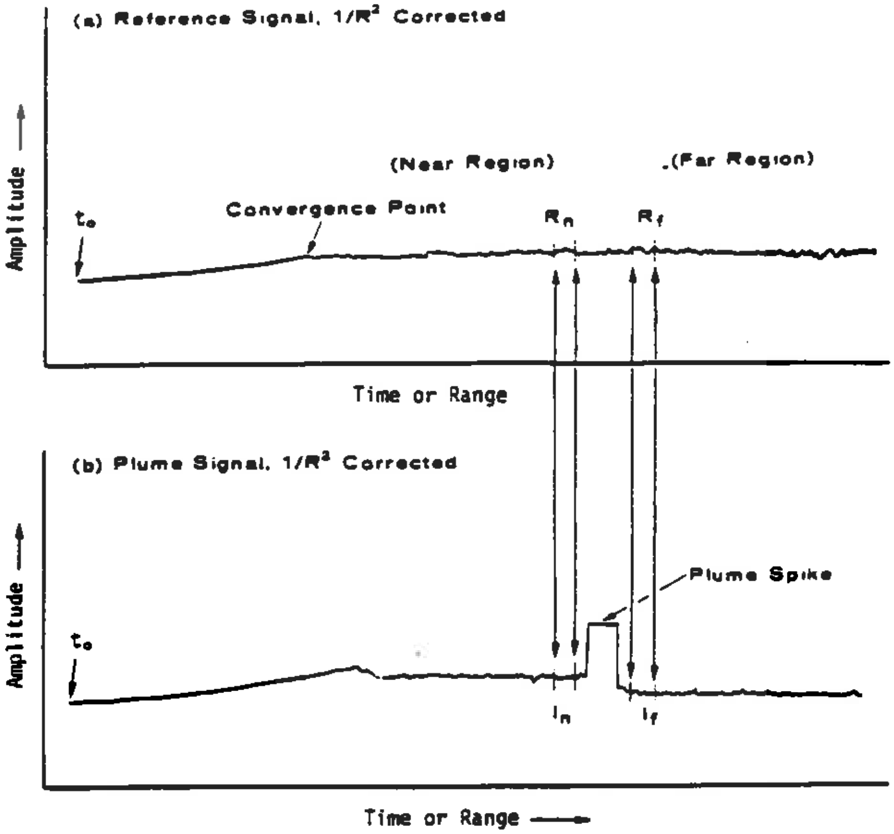
R_f=far-region pick interval signal amplitude, reference signal, $1/R^2$ corrected.

The $1/R^2$ correction to the plume and reference signal amplitudes is made by multiplying the amplitude for each successive sample interval from the time reference, by the square of the lidar time (or range) associated with that sample interval [Reference 5.1].

The first step in selecting the pick intervals for Equation AM1-2 is to divide the plume signal amplitude by the reference signal amplitude at the same respective ranges to obtain a "normalized" signal. The pick intervals selected using this normalized signal, are a minimum of 15 m (100 nanoseconds) in length and consist of at least 5 contiguous sample intervals. In addition, the following criteria, listed in order of importance, govern pick interval selection. (1) The intervals shall be in a region of the normalized signal where the reference signal meets the requirements of Section 2.3 and is everywhere greater than zero. (2) The intervals (near and far) with the minimum average amplitude are chosen. (3) If more than one interval with the same minimum average amplitude is found, the interval closest to the plume is chosen. (4) The standard deviation, S_o, for the calculated opacity shall be 8% or less. (S_o is calculated by Equation AM1-7).

If S_o is greater than 8%, then the far pick interval shall be changed to the next interval of minimal average amplitude. If S_o is still greater than 8%, then this procedure is repeated for the far pick interval. This procedure may be repeated once again for the near pick interval, but if S_o remains greater than 8%, the plume signal shall be discarded.

The reference signal pick intervals, R_n and R_f, must be chosen over the same time interval as the plume signal pick intervals, I_n and I_f, respectively [Figure AM1-III]. Other methods of selecting pick intervals may be used if they give equivalent results. Field-oriented examples of pick interval selection are available in Reference 5.1.



(a) Reference signal, $1/R^2$-corrected. This reference signal is for plume signal (b). R_n, R_f are chosen to coincide with I_n, I_f.

(b) Plume signal, $1/R^2$-corrected. The plume spike and the decrease in the backscatter signal amplitude in the far region are due to the opacity of the plume. I_n, I_f are chosen as indicated in Section 2.6.

Figure AM1-III. Plots of Lidar Backscatter Signals

The average amplitudes for each of the pick intervals, I_n, I_f, R_n, R_f, shall be calculated by averaging the respective individual amplitudes of the sample intervals from the plume signal and the associated reference signal each corrected for $1/R^2$. The amplitude of I_n shall be calculated according to Equation (AM-3).

$$I_n = \frac{1}{m}\sum_{i=1}^{m} I_{ni}\,, \qquad \text{(AM1-3)}$$

where:

I_{ni}=the amplitude of the ith sample interval (near-region),

Σ=sum of the individual amplitudes for the sample intervals,

m=number of sample intervals in the pick interval, and

I_n=average amplitude of the near-region pick interval.

Similarly, the amplitudes for I_f, R_n, and R_f are calculated with the three expressions in Equation (AM1-4).

$$I_f = \frac{1}{m} \sum_{i=1}^{m} I_{fi} , \quad R_n = \frac{1}{m} \sum_{i=1}^{m} R_{ni} , \quad R_f = \frac{1}{m} \sum_{i=1}^{m} R_{fi} \tag{AM1-4}$$

The standard deviation, S_{In}, of the set of amplitudes for the near-region pick interval, I_n, shall be calculated using Equation (AM1-5).

$$S_{In} = \left[\sum_{i=1}^{m} \frac{(I_{ni} - I_n)^2}{(m-1)} \right]^{\frac{1}{2}} . \tag{AM1-5}$$

Similarly, the standard deviations S_{If}, S_{Rn}, and S_{Rf} are calculated with the three expressions in Equation (AM1-6).

$$S_{If} = \left[\sum_{i=1}^{m} \frac{(I_{fi} - I_f)^2}{(m-1)} \right]^{\frac{1}{2}}$$

$$S_{Rn} = \left[\sum_{i=1}^{m} \frac{(R_{ni} - R_n)^2}{(m-1)} \right]^{\frac{1}{2}} ,$$

$$S_{Rf} = \left[\sum_{i=1}^{m} \frac{(R_{fi} - R_f)^2}{(m-1)} \right]^{\frac{1}{2}} \tag{AM1-6}$$

The standard deviation S_o, for each associated opacity value, O_p, shall be calculated using Equation (AMI-7).

$$S_o = \frac{(100\%)}{2} \left(\frac{I_f}{R_f} \frac{R_n}{I_n} \right)^{\frac{1}{2}} \left[\frac{S_{In}^{\ 2}}{I_n^{\ 2}} + \frac{S_{If}^{\ 2}}{I_f^{\ 2}} + \frac{S_{Rn}^{\ 2}}{R_n^{\ 2}} + \frac{S_{Rf}^{\ 2}}{R_f^{\ 2}} \right]^{\frac{1}{2}} \tag{AM1-7}$$

The calculated values of I_n, I_f, R_n, R_f, S_{In}, S_{If}, S_{Rn}, S_{Rf}, O_p, and S_o should be recorded. Any plume signal with an S_o greater than 8% shall be discarded.

2.6.1 Azimuth Angle Correction. If the azimuth angle correction to opacity specified in this section is performed, then the elevation angle correction specified in Section 2.6.2 shall not be performed. When opacity is measured in the residual region of an attached steam plume, and the lidar line-of-sight is not perpendicular to the plume, it may be necessary to correct the opacity measured by the lidar to obtain the opacity that would be measured on a path perpendicular to the plume. The following method, or any other method which produces equivalent results, shall be used to determine the need for a correction, to calculate the correction, and to document the point within the plume at which the opacity was measured.

Figure AM1-IV(b) shows the geometry of the opacity correction. L' is the path through the plume along which the opacity measurement is made. P' is the path perpendicular to the plume at the same point. The angle ϵ is the angle between L' and the plume center line. The angle $(\pi/2-\epsilon)$, is the angle between the L' and P'. The measured opacity, O_p, measured along the path L' shall be corrected to obtain the corrected opacity, O_{pc}, for the path P', using Equation (AM1-8).

$$\begin{aligned} O_{pc} &= (100\%) \left[1 - (1 - 0.01\, O_p)^{\mathrm{Cos}\ (\pi/2-\varepsilon)} \right] \\ &= (100\%) \left[1 - (1 - 0.01\, O_p)^{\mathrm{Sin}\ \varepsilon} \right] \end{aligned} \tag{AM1-8}$$

The correction in Equation (AM1-8) shall be performed if the inequality in Equation (AM1-9) is true.

$$\varepsilon \geq \operatorname{Sin}^{-1}\left[\frac{\ln(101 - O_p)}{\ln(100 - O_p)}\right] \qquad \text{(AM1-9)}$$

Figure AM1-IV(a) shows the geometry used to calculate ε and the position in the plume at which the lidar measurement is made. This analysis assumes that for a given lidar measurement, the range from the lidar to the plume, the elevation angle of the lidar from the horizontal plane, and the azimuth angle of the lidar from an arbitrary fixed reference in the horizontal plane can all be obtained directly.

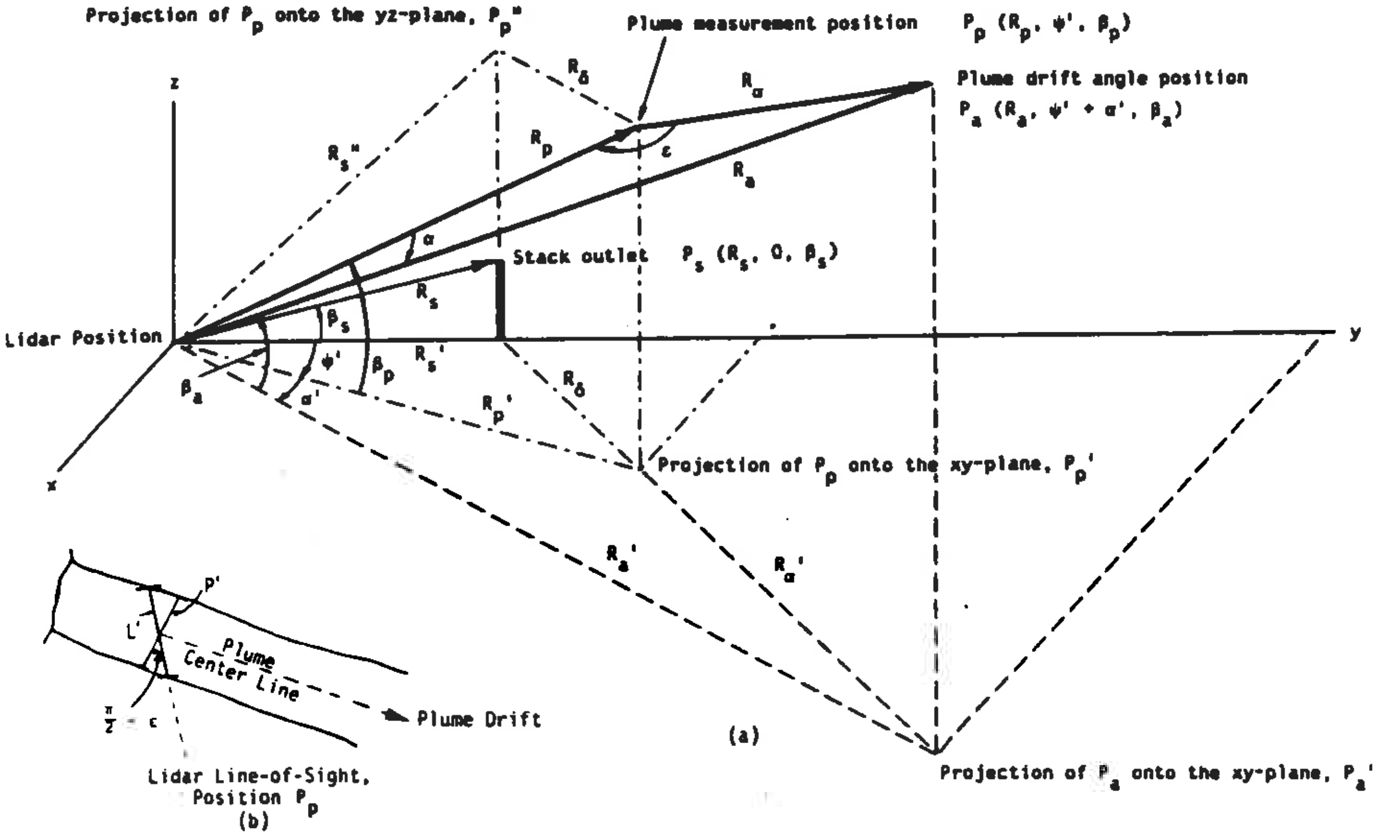


Figure AMI - IV. Correction in Opacity for Drift of the Residual Region of an Attached Steam Plume.

R_s = range from lidar to source*
β_s = elevation angle of R_s*
R_p = range from lidar to plume at the opacity measurement point*
β_p = elevation angle of R_p*
R_a = range from lidar to plume at some arbitrary point, P_a, so the drift angle of the plume can be determined*
β_a = elevation angle of R_a*
α = angle between R_p and R_a
R'_s = projection of R_s in the horizontal plane
R'_p = projection of R_p in the horizontal plane
R'_a = projection of R_a in the horizontal plane
ψ' = angle between R'_s and R'_p*
α' = angle between R'_p and R'_a*
R_δ = distance from the source to the opacity measurement point projected in the horizontal plane
R_θ = distance from opacity measurement point P_p to the point in the plume P_a.

$$O_{pc} = 1 - (1 - O_p)^{\mathrm{Cos}\ (\pi/2 - \varepsilon)} = 1 - (1 - O_p)^{\mathrm{Sin}\ \varepsilon} \qquad \text{(AMI-8)}$$

The correction angle ϵ shall be determined using Equation AM1-10.
where:
$\alpha = \mathrm{Cos}^{-1}(\mathrm{Cos}\beta_p\ \mathrm{Cos}\beta_s\ \mathrm{Cos}\alpha' + \mathrm{Sin}\beta_p\ \mathrm{Sin}\beta_s)$,
and
$R\theta = (R_p^2 + R_s^2 - 2\ R_p\ R_s\ \mathrm{Cos}\alpha)^{1/2}$

R_δ, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1-11.

$$R_\delta = (R_s'^2 + R_p'^2 - 2R_s'R_p'\mathrm{Cos}\psi')^{\frac{1}{2}}\ , \qquad \text{(AM1-11)}$$

where:
$R'_s = R_s\ \mathrm{Cos}\ \beta_s$, and
$R'_p = R_p\ \mathrm{Cos}\ \beta_p$.

In the special case where the plume centerline at the opacity measurement point is horizontal, parallel to the ground, Equation AM1-12 may be used to determine ϵ instead of Equation AM1-10.

$$\varepsilon = \mathrm{Cos}^{-1}\left[\frac{R_p{}^2 + R_\delta{}^2 - R_s''^2}{2\ R_p\ R_\delta}\right] \qquad \text{(AM1-12)}$$

where:
$R''_s = (R'^2_s + R_p^2\ \mathrm{Sin}^2\ \beta_p)^{1/2}$.

If the angle ϵ is such that $\epsilon < 30°$ or $\epsilon > 150°$, the azimuth angle correction shall not be performed and the associated opacity value shall be discarded.

2.6.2 Elevation Angle Correction. An individual lidar-measured opacity, O_p, shall be corrected for elevation angle if the laser elevation or inclination angle, β_p [Figure AM1-V], is greater than or equal to the value calculated in Equation AM1-13.

$$\beta_p \geq \mathrm{Cos}^{-1}\left[\frac{\ln\ (101 - O_p)}{\ln\ (100 - O_p)}\right] \qquad \text{(AM1-13)}$$

The measured opacity, O_p, along the lidar path L is adjusted to obtain the corrected opacity, O_{pc}, for the actual plume (horizontal) path, P, by using Equation (AM1-14).

$$O_{pc} = (100\%)\left[1 - (1 - 0.01\ O_p)^{\mathrm{Cos}\beta_p}\right], \qquad \text{(AM1-14)}$$

where:
β_p = lidar elevation or inclination angle,
O_p = measured opacity along path L, and
O_{pc} = corrected opacity for the actual plume thickness P.

The values for β_p, O_p and O_{pc} should be recorded.

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*Obtained directly from lidar. These values should be recorded.

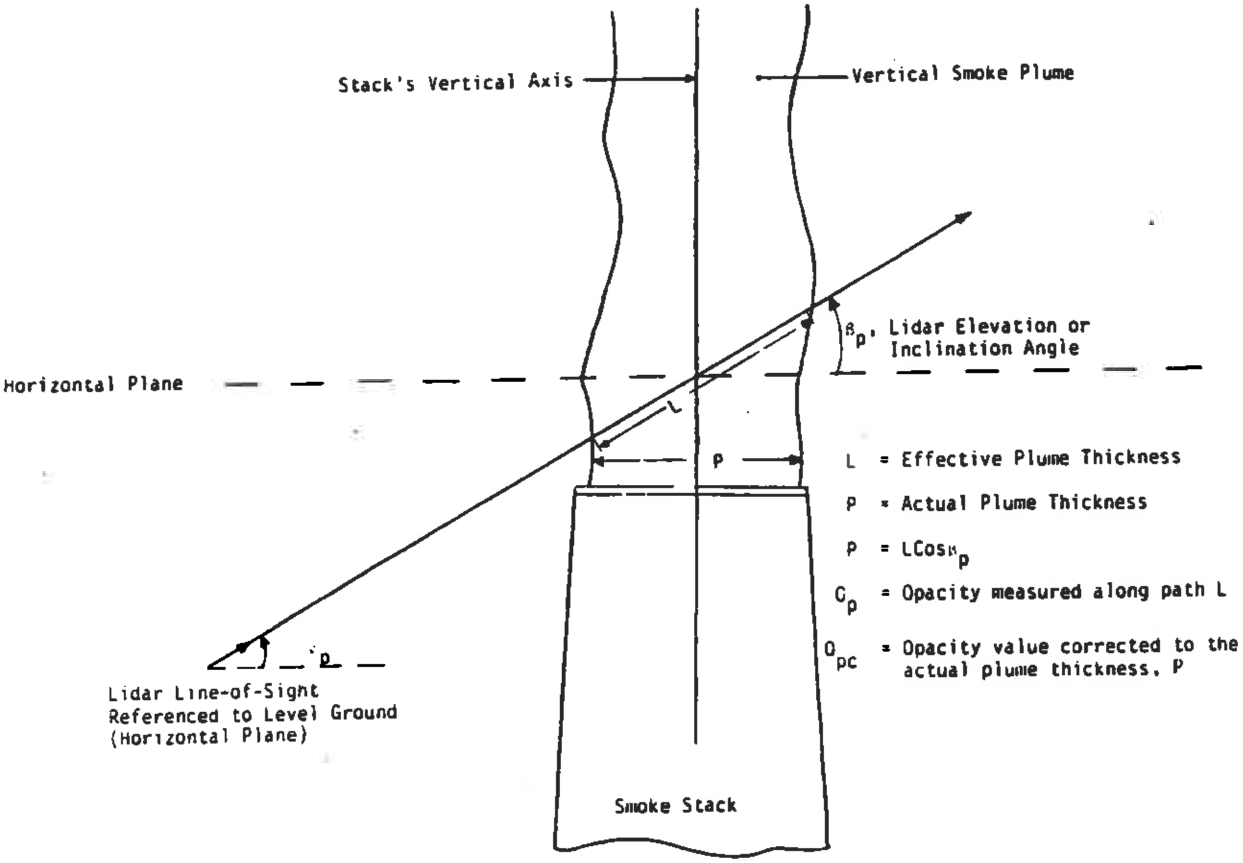


Figure AM1-V. Elevation Angle Correction for Vertical Plumes.

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1-15.

$$O_{pa} = O_{pc} - [2\ S_o + 5\%]. \qquad \text{(AM1-15)}$$

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, $\bar{O}_{pa}$, shall be calculated as the average of the consecutive individual actual opacity values, O_{pa}, by Equation AM1-16.

$$\bar{O}_{pa} = \frac{1}{n} \sum_{k=1}^{n} (O_{pa})_k \qquad \text{(AM1-16)}$$

where:

$(O_{pa})_k$=the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

Σ=the sum of the individual actual opacity values.

n=the number of individual actual opacity values contained in the averaging interval.

$\bar{O}_{pa}$=average actual opacity calculated over the averaging interval.

3. Lidar Performance Verification. The lidar shall be subjected to two types of performance verifications that shall be peformed in the field. The annual calibration, conducted at least once a year, shall be used to directly verify operation and performance of the entire lidar system. The routine verification, conducted for each emission source measured, shall be used to insure proper performance of the optical receiver and associated electronics.

3.1 Annual Calibration Procedures. Either a plume from a smoke generator or screen targets shall be used to conduct this calibration.

If the screen target method is selected, five screens shall be fabricated by placing an opaque mesh material over a narrow frame (wood, metal extrusion, etc.). The screen shall have a surface area of at least one square meter. The screen material should be chosen for precise optical opacities of about 10, 20, 40, 60, and 80%. Opacity of each target shall be optically determined and should be recorded. If a smoke generator plume is selected, it shall meet the requirements of Section 3.3 of Reference Method 9. This calibration shall be performed in the field during calm (as practical) atmospheric conditions. The lidar shall be positioned in accordance with Section 2.1.

The screen targets must be placed perpendicular to and coincident with the lidar line-of-sight at sufficient height above the ground (suggest about 30 ft) to avoid ground-level dust contamination. Reference signals shall be obtained just prior to conducting the calibration test.

The lidar shall be aimed through the center of the plume within 1 stack diameter of the exit, or through the geometric center of the screen target selected. The lidar shall be set in operation for a 6-minute data run at a nominal pulse rate of 1 pulse every 10 seconds. Each backscatter return signal and each respective opacity value obtained from the smoke generator transmissometer, shall be obtained in temporal coincidence. The data shall be analyzed and reduced in accordance with Section 2.6 of this method. This calibration shall be performed for 0% (clean air), and at least five other opacities (nominally 10, 20, 40, 60, and 80%).

The average of the lidar opacity values obtained during a 6-minute calibration run shall be calculated and should be recorded. Also the average of the opacity values obtained from the smoke generator transmissometer for the same 6-minute run shall be calculated and should be recorded.

Alternate calibration procedures that do not meet the above requirements but produce equivalent results may be used.

3.2 Routine Verification Procedures. Either one of two techniques shall be used to conduct this verification. It shall be performed at least once every 4 hours for each emission source measured. The following parameters shall be directly verified.

1) The opacity value of 0% plus a minimum of 5 (nominally 10, 20, 40, 60, and 80%) opacity values shall be verified through the PMT detector and data processing electronics.

2) The zero-signal level (receiver signal with no optical signal from the source present) shall be inspected to insure that no spurious noise is present in the signal. With the entire lidar receiver and analog/digital electronics turned on and adjusted for normal operating performance, the following procedures shall be used for Techniques 1 and 2, respectively.

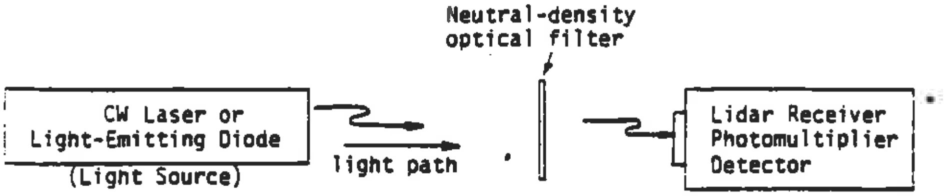
3.2.1 Procedure for Technique 1. This test shall be performed with no ambient or stray light reaching the PMT detector. The narrow band filter (694.3 nanometers peak) shall be removed from its position in front of the PMT detector. Neutral density filters of nominal opacities of 10, 20, 40, 60, and 80% shall be used. The recommended test configuration is depicted in Figure AM1-VI.

The zero-signal level shall be measured and should be recorded, as indicated in Figure AM1-VI(a). This simulated clear-air or 0% opacity value shall be tested in using the selected light source depicted in Figure AM1-VI(b).

The light source either shall be a continuous wave (CW) laser with the beam mechanically chopped or a light emitting diode controlled with a pulse generator (rectangular pulse). (A laser beam may have to be attenuated so as not to saturate the PMT detector). This signal level shall be measured and should be recorded. The opacity value is calculated by taking two pick intervals [Section 2.6] about 1 microsecond apart in time and using Equation (AM1-2) setting the ratio $R_n/R_f=1$. This calculated value should be recorded.

(a) Zero-Signal Level Test

(b) Clear-Air or 0% Opacity Test



(c) Optical Filter Test (simulated opacity values)

*Tests shall be performed with no ambient or stray light reaching the detector.

Figure AM1-VI. Test Configuration for Technique 1.

The simulated clear-air signal level is also employed in the optical test using the neutral density filters. Using the test configuration in Figure AM1-VI(c), each neutral density filter shall be separately placed into the light path from the light source to the PMT detector. The signal level shall be measured and should be recorded. The opacity value for each filter is calculated by taking the signal level for that respective filter (L_i), dividing it by the 0% opacity signal level (L_o) and performing the remainder of the calculation by Equation (AM1-2) with $R_n/R_f=1$. The calculated opacity value for each filter should be recorded.

The neutral density filters used for Technique 1 shall be calibrated for actual opacity with accuracy of ±2% or better. This calibration shall be done monthly while the filters are in use and the calibrated values should be recorded.

3.2.2 Procedure for Technique 2. An optical generator (built-in calibration mechanism) that contains a light-emitting diode (red light for a lidar containing a ruby laser) is used. By injecting an optical signal into the lidar receiver immediately ahead of the PMT detector, a backscatter signal is simulated. With the entire lidar receiver electronics turned on and adjusted for normal operating performance, the optical generator is turned on and the simulation signal (corrected for $1/R^2$) is selected with no plume spike signal and with the opacity value equal to 0%. This simulated clear-air atmospheric return signal is displayed on the system's video display. The lidar operator then makes any fine adjustments that may be necessary to maintain the system's normal operating range.

The opacity values of 0% and the other five values are selected one at a time in any order. The simulated return signal data should be recorded. The opacity value shall be calculated. This measurement/calculation shall be performed at least three times for each selected opacity value. While the order is not important, each of the opacity values from the optical generator shall be verified. The calibrated optical generator opacity value for each selection should be recorded.

The optical generator used for Technique 2 shall be calibrated for actual opacity with an accuracy of ±1% or better. This calibration shall be done monthly while the generator is in use and calibrated value should be recorded.

Alternate verification procedures that do not meet the above requirements but produce equivalent results may be used.

3.3 Deviation. The permissible error for the annual calibration and routine verification are:

3.3.1 Annual Calibration Deviation.

3.3.1.1 Smoke Generator. If the lidar-measured average opacity for each data run is not within ±5% (full scale) of the respective smoke generator's average opacity over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.1.2 Screens. If the lidar-measured average opacity for each data run is not within ±3% (full scale) of the laboratory-determined opacity for each respective simulation screen target over the range of 0% through 80%, then the lidar shall be considered out of calibration.

3.3.2 Routine Verification Error. If the lidar-measured average opacity for each neutral density filter (Technique 1) or optical generator selection (Technique 2) is not within ±3% (full scale) of the respective laboratory calibration value then the lidar shall be considered non-operational.

4. Performance/Design Specification for Basic Lidar System.

4.1 Lidar Design Specification. The essential components of the basic lidar system are a pulsed laser (transmitter), optical receiver, detector, signal processor, recorder, and an aiming device that is used in aiming the lidar transmitter and receiver. Figure AM1-VII shows a functional block diagram of a basic lidar system.

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in Section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete runs and the results of each should be recorded. The requirements of Section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of Section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References.

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO, EPA-330/1-79-003-R, Arthur W. Dybdahl, current edition [NTIS No. PB81-246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO, EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742, August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA-650/4-73-002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1-176, 8 March 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

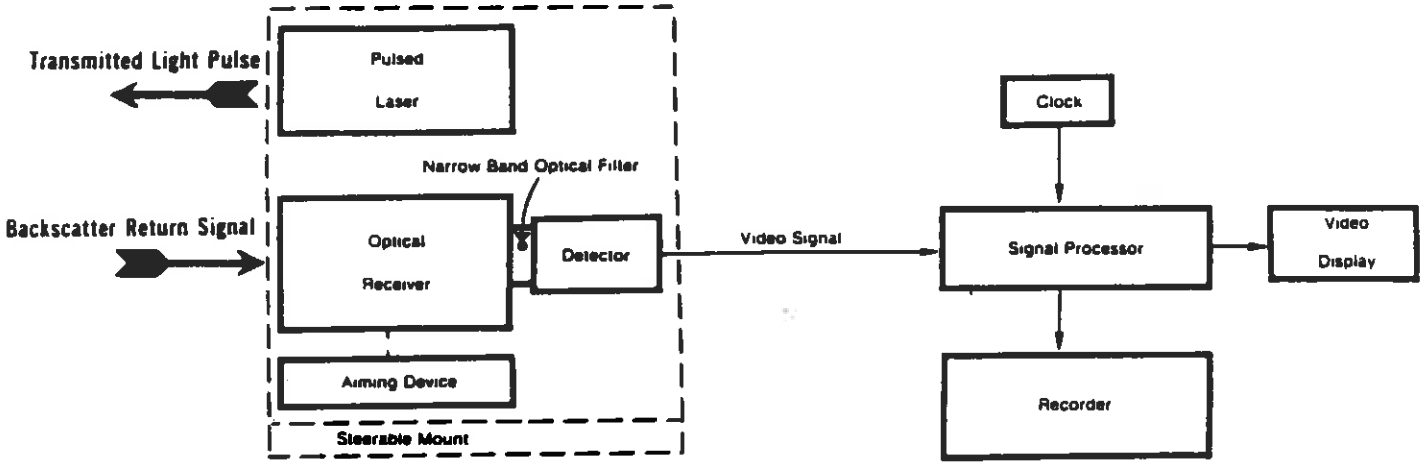


Figure AM1-VII. Functional Block Diagram of a Basic Lidar System

METHOD 10—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 *Principle.* An integrated or continuous gas sample is extracted from a sampling point and analyzed for carbon monoxide (CO) content using a Luft-type nondispersive infrared analyzer (NDIR) or equivalent.

1.2 *Applicability.* This method is applicable for the determination of carbon monoxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The test procedure will indicate whether a continuous or an integrated sample is to be used.

2. *Range and sensitivity.*

2.1 *Range.* 0 to 1,000 ppm.

2.2 *Sensitivity.* Minimum detectable concentration is 20 ppm for a 0 to 1,000 ppm span.

3. *Interferences.* Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. *Precision and accuracy.*

4.1 *Precision.* The precision of most NDIR analyzers is approximately ±2 percent of span.

4.2 *Accuracy.* The accuracy of most NDIR analyzers is approximately ±5 percent of span after calibration.

5. *Apparatus.*

5.1 *Continuous sample* (Figure 10-1).

5.1.1 *Probe.* Stainless steel or sheathed Pyrex[1] glass, equipped with a filter to remove particulate matter.

5.1.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2 *Integrated sample* (Figure 10-2).

5.2.1 *Probe.* Stainless steel or sheathed Pyrex glass, equipped with a filter to remove particulate matter.

5.2.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2.3 *Valve.* Needle valve, or equivalent, to to adjust flow rate.

5.2.4 *Pump.* Leak-free diaphragm type, or equivalent, to transport gas.

5.2.5 *Rate meter.* Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per min. (0.035 cfm).

5.2.6 *Flexible bag.* Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft³). Leak-test the bag in the laboratory before using by evacuating bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

5.2.7 *Pitot tube.* Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with the time or a sample traverse is conducted.

5.3 *Analysis* (Figure 10-3).

5.3.1 *Carbon monoxide analyzer.* Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

5.3.2 *Drying tube.* To contain approximately 200 g of silica gel.

5.3.3 *Calibration gas.* Refer to section 6.1.

5.3.4 *Filter.* As recommended by NDIR manufacturer.

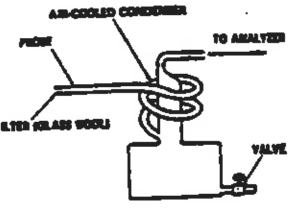


Figure 10-1. Continuous sampling train.

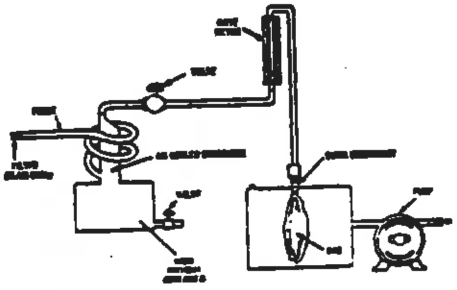


Figure 10-2. Integrated gas-sampling train.

5.3.5 CO_2 *removal tube.* To contain approximately 500 g of ascarite.

5.3.6 *Ice water bath.* For ascarite and silica gel tubes.

5.3.7 *Valve.* Needle valve, or equivalent, to adjust flow rate.

5.3.8 *Rate meter.* Rotameter or equivalent to measure gas flow rate of 0 to 1.0 liter per min. (0.035 cfm) through NDIR.

5.3.9 *Recorder (optional).* To provide permanent record of NDIR readings.

6. *Reagents.*

6.1 *Calibration gases.* Known concentration of CO in nitrogen (N_2) for instrument span, prepurified grade of N_2 for zero, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.

6.2 *Silica gel.* Indicating type, 6 to 16 mesh, dried at 175° C (347° F) for 2 hours.

6.3 *Ascarite.* Commercially available.

7. *Procedure.*

7.1 *Sampling.*

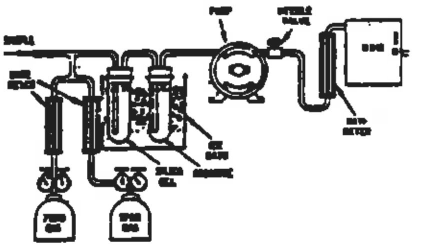


Figure 10-3. Analytical equipment.

7.1.1 *Continuous sampling.* Set up the equipment as shown in Figure 10-1 making sure all connections are leak free. Place the probe in the stack at a sampling point and purge the sampling line. Connect the analyzer and begin drawing sample into the analyzer. Allow 5 minutes for the system to stabilize, then record the analyzer reading as required by the test procedure. (See section 7.2 and 8). CO_2 content of the gas may be determined by using the Method 3 integrated sample procedure or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 *Integrated sampling.* Evacuate the flexible bag. Set up the equipment as shown in Figure 10-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.2 *CO Analysis.* Assemble the apparatus as shown in Figure 10-3, calibrate the instrument, and perform other required operations as described in section 8. Purge analyzer with N_2 prior to introduction of each sample. Direct the sample stream through the instrument for the test period, recording the readings. Check the zero and span again after the test to assure that any drift or malfunction is detected. Record the sample data on Table 10-1.

8. *Calibration.* Assemble the apparatus according to Figure 10-3. Generally an instrument requires a warm-up period before stability is obtained. Follow the manufacturer's instructions for specific procedure. Allow a minimum time of 1 hour for warm-up. During this time check the sample conditioning apparatus, i.e., filter, condenser, drying tube, and CO_2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen and the calibration gases.

TABLE 10-1—FIELD DATA

Comments

Location__________

Test__________

Date__________

Operator__________

Clock time	Rotameter setting, liters per minute (cubic feet per minute)

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

9. *Calculation—Concentration of carbon monoxide.* Calculate the concentration of carbon monoxide in the stack using equation 10-1.

$$C_{CO\ stack} = C_{CO\ NDIR}(1 - F_{CO_2})$$

where:

$C_{CO\ stack}$ = concentration of CO in stack, ppm by volume (dry basis).

$C_{CO\ NDIR}$ = concentration of CO measured by NDIR analyzer, ppm by volume (dry basis).

F_{CO_2} = volume fraction of CO_2 in sample, i.e., percent CO_2 from Orsat analysis divided by 100.

10. *Alternative Procedures*

10.1 Interference Trap. The sample conditioning system described in Method 10A, sections 2.1.2 and 4.2, may be used as an alternative to the silica gel and ascarite traps.

11. ***Bibliography.***

11.1 McElroy, Frank. The Intertech NDIR-CO Analyzer. Presented at 11th Methods Conference on Air Pollution, University of California, Berkeley, Calif., April 1, 1970.

11.2 Jacobs, M. B., et al., Continuous Determination of Carbon Monoxide and Hydrocarbons in Air by a Modified Infrared Analyzer, J. Air Pollution Control Association, 9(2): 110-114, August 1959.

11.3 MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Technical Products Division, Pittsburgh, Pa.

11.4 Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instruments, Inc., Beckman Instructions 1635-B, Fullerton, Calif., October 1967.

11.5 Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton, N.J.

11.6 UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, West Virginia.

ADDENDA—A. PERFORMANCE SPECIFICATIONS FOR NDIR CARBON MONOXIDE ANALYZERS.

Range (minimum)	0–1000 ppm.
Output (minimum)	0–10mV.
Minimum detectable sensitivity.	20 ppm.
Rise time, 90 percent (maximum).	30 seconds.
Fall time, 90 percent (maximum).	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	10% in 8 hours.
Precision (minimum)	±2% of full scale.
Noise (maximum)	±1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO_2—1000 to 1, H_2O—500 to 1.

B. *Definitions of Performance Specifications.*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full scale—The maximum measuring limit for a given range.

Minimum detectable sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Time to 90 percent response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

METHOD 12—DETERMINATION OF INORGANIC LEAD EMISSIONS FROM STATIONARY SOURCES

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of inorganic lead (Pb) emissions from specified stationary sources only.

1.2 Principle. Particulate and gaseous Pb emissions are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame.

2. *Range, Sensitivity, Precision, and Interferences.*

2.1 Range. For a minimum analytical accuracy of ±10 percent, the lower limit of the range is 100 μg. The upper limit can be considerably extended by dilution.

2.2 Analytical Sensitivity. Typical sensitivities for a 1-percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines, respectively.

2.3 Precision. The within-laboratory precision, as measured by the coefficient of variation ranges from 0.2 to 9.5 percent relative to a run-mean concentration. These values were based on tests conducted at a gray iron foundry, a lead storage battery manufacturing plant, a secondary lead smelter, and a lead recovery furnace of an alkyl lead manufacturing plant. The concentrations encountered during these tests ranged from 0.61 to 123.3 mg Pb/m^3.

2.4 Interferences. Sample matrix effects may interfere with the analysis for Pb by flame atomic absorption. If this interference is suspected, the analyst may confirm the presence of these matrix effects and frequently eliminate the interference by using the Method of Standard Additions.

High concentrations of copper may interfere with the analysis of Pb at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

3. *Apparatus.*

3.1 Sampling Train. A schematic of the sampling train is shown in Figure 12-1; it is similar to the Method 5 train. The sampling train consists of the following components:

3.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1 to 2.1.6 and 2.1.8 to 2.1.10, respectively.

3.1.2 Impingers. Four impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. For the second impinger, use the Greenburg-Smith design with the standard tip. Place a thermometer, capable of measuring temperature to within 1°C (2°F) at the outlet of the fourth impinger for monitoring purposes.

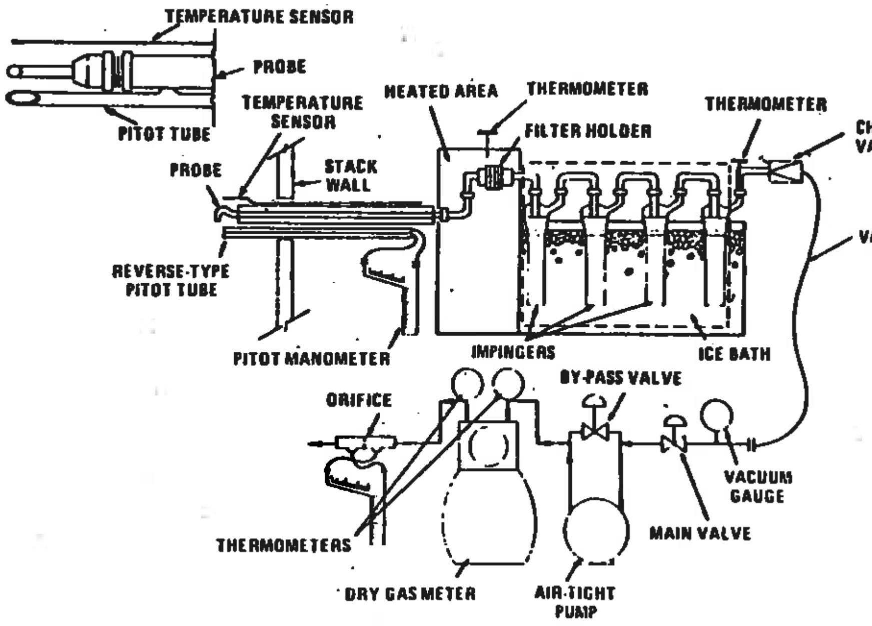

Figure 12-1. Inorganic lead sampling train.

3.2 Sample Recovery. The following items are needed:

3.2.1 Probe-Liner and Probe-Nozzle Brushes, Petri Dishes, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.6, and 2.2.7, respectively.

3.2.2 Wash Bottles. Glass (2).

3.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for 0.1 nitric acid (HNO_3) impinger and probe solutions and washes, 1000-ml. Use screw-cap liners that are either rubber-backed Teflon* or leak-free and resistant to chemical attack by 0.1 N HNO_3. (Narrow mouth glass bottles have been found to be less prone to leakage.)

3.2.4 Graduated Cylinder and/or Balance. To measure condensed water to within 2 ml or 1 g. Use a graduated cylinder that has a minimum capacity of 500 ml, and subdivisions no greater than 5 ml. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less.)

3.2.5 Funnel. Glass, to aid in sample recovery.

3.3 Analysis. The following equipment is needed:

3.3.1 Atomic Absorption Spectrophotometer. With lead hollow cathode lamp and burner for air/acetylene flame.

3.3.2 Hot Plate.

3.3.3 Erlenmeyer Flasks. 125-ml, 24/40 $.

3.3.4 Membrane Filters. Millipore SCWPO 4700 or equivalent.

3.3.5 Filtration Apparatus. Millipore vacuum filtration unit, or equivalent, for use with the above membrane filter.

3.3.6 Volumetric Flasks. 100-ml, 250-ml, and 1000-ml.

4. *Reagents.*

4.1 Sampling. The reagents used in sampling are as follows:

4.1.1 Filter. Gelman Spectro Grade, Reeve Angel 934 AH, MSA 1106 BH, all with lot assay for Pb, or other high-purity glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. Conduct the filter efficiency test using ASTM Standard Method D2986-71 (incorporated by reference—see § 60.17) or use test data from the supplier's quality control program.

4.1.2 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Section 3.1.2, 3.1.4, and 3.1.5, respectively.

4.1.3 Water. Deionized distilled, to conform to ASTM Specification D1193-77 (incorporated by reference—see § 60.17), Type 3. If high concentrations of organic matter

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*Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

4.1.4 Nitric Acid, 0.1 N. Dilute 6.5 ml of concentrated HNO_3 to 1 liter with deionized distilled water. (It may be desirable to run blanks before field use to eliminate a high blank on test samples.)

4.2 Pretest Preparation. 6 N HNO_3 is needed. Dilute 390 ml of concentrated HNO_3 to 1 liter with deionized distilled water.

4.3 Sample Recovery. 0.1 N HNO_3 (same as 4.1.4 above) is needed for sample recovery.

4.4 Analysis. The following reagents are needed for analysis (use ACS reagent grade chemicals or equivalent, unless otherwise specified):

4.4.1 Water. Same as 4.1.3 above.

4.4.2 Nitric Acid. Concentrated.

4.4.3 Nitric Acid, 50 percent (V/V). Dilute 500 ml of concentrated HNO_3 to 1 liter with deionized distilled water.

4.4.4 Stock Lead Standard Solution, 1000 μg Pb/ml. Dissolve 0.1598 g of lead nitrate [$Pb(NO_3)_2$] in about 60 ml of deionized distilled water, add 2 ml concentrated HNO_3, and dilute to 100 ml with deionized distilled water.

4.4.5 Working Lead Standards. Pipet 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the stock lead standard solution (4.4.4) into 250-ml volumetric flasks. Add 5 ml of concentrated HNO_3 to each flask and dilute to volume with deionized distilled water. These working standards contain 0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 μg Pb/ml, respectively. Prepare, as needed, additional standards at other concentrations in a similar manner.

4.4.6 Air. Suitable quality for atomic absorption analysis.

4.4.7 Acetylene. Suitable quality for atomic absorption analysis.

4.4.8 Hydrogen Peroxide, 3 percent (V/V). Dilute 10 ml of 30 percent H_2O_2 to 100 ml with deionized distilled water.

5. *Procedure.*

5.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

5.1.2 Preliminary Determinations. Follow the same general procedure given in Method 5, Section 4.1.2.

5.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 ml of 0.1 HNO_3 in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Set up the train as shown in Figure 12-1.

5.1.4 Leak-Check Procedures. Follow the general leak-check procedures given in Method 5, Sections 4.1.4.1. (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

5.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in EPA Method 5, Figure 5-2.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 *Sample Recovery.* Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sapling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the glassware inlet where the probe was fastened and cap the inlet. Remove the umbilical cord from the last impinger and cap the impinger. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to a cleanup area, which is clean and protected from the wind so that the chances of contaminating or losing the sample are minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

5.2.1 *Container No. 1* (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. If it is necessary to fold the filter, do so such that the sample-exposed side is inside the fold. Carefully transfer to the petri dish any visible sample matter and/or filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

5.2.2 *Container No. 2* (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover sample matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 0.1 N HNO_3 and placing the wash into a glass sample storage container. Measure and record (to the nearest 2-ml) the total amount of 0.1 N HNO_3 used for each rinse. Perform the 0.1 N HNO^3 rinses as follows:

Carefully remove the probe nozzle and rinse the inside surfaces with 0.1 N HNO^3 from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO_3 rinse shows no visible particles, then make a final rinse of the inside surface.

Brush and rinse with 0.1 N HNO_3 the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with 0.1 N HNO_3. While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO_3, tilt the probe and squirt 0.1 N HNO_3 into its upper end. Let the 0.1 N HNO_3 drain from the lower end into the sample container. The tester may use a glass funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, squirt 0.1 N HNO_3 into the upper end of the probe as the probe brush is being pushed with a twisting action through the probe; hold the sample container underneath the lower end of the probe and catch any 0.1 N HNO_3 and sample matter that is brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N HNO_3 and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which sample matter can be entrapped. Rinse the brush with 0.1 N HNO_3 and quantitatively collect these washings in the sample container. After the brushing make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize loss of sample. Between sampling runs, keep brushes clean and protected from contamination.

After insuring that all joints are wiped clean of silicone grease, brush and rinse with 0.1 N HNO_3 the inside of the front half of the filter holder. Brush and rinse each suface three times or more, if needed, to remove visible sample matter. Make a final rinse of the brush and filter holder. After all 0.1 N HNO_3 washings and sample matter are collected in the sample container, tighten the lid on the sample container so that the fluid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

5.2.3 *Container No. 3* (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow procedure for Container No. 3 under Section 5.4 (Analysis).

5.2.4 *Container No. 4* (Impingers). Due to the large quantity of liquid involved, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease and cap the joints.
2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.
3. Transfer the contents of the impingers to a 500-ml graduated cylinder. Remove the outlet ball joint cap and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within ±2 ml. Alternatively, determine the weight of the liquid to within ±0.5 g. Record in the log the volume or weight of the liquid present, along with a notation of any color or film observed in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).
4. Transfer the contents to Container No. 4.

5. Note: In steps 5 and 6 below, measure and record the total amount of 0.1 N HNO_3 used for rinsing. Pour approximately 30 ml of 0.1 N HNO_3 into each of the first three impingers and agitate the impingers. Drain the 0.1 N HNO_3 through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N HNO_3; transfer this rinse into Container No. 4. (*Do not rinse or brush the glass-fritted filter support.*) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

5.2.5 Blanks. Save 200 ml of the 0.1 N HNO_3 used for sampling and cleanup as a blank. Take the solution directly from the bottle being used and place into a glass sample container labeled "0.1 N HNO_3 blank."

5.3 Sample Preparation.

5.3.1 *Container No. 1* (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-ml Erlenmeyer flask. Rinse the petri dish with 10 ml of 50 percent HNO_3 to insure a quantitative transfer and add to the flask. (Note: If the total volume required in Section 5.3.3 is expected to exceed 80 ml, use a 250-ml Erlenmeyer flask in place of the 125-ml flask.)

5.3.2 *Containers No. 2 and No. 4* (Probe and Impingers). (Check the liquid level in Containers No. 2 and/or No. 4 and confirm as to whether or not leakage occurred during transport; note observation on the analysis sheet. If a noticeable amount of leakage had occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.) Combine the contents of Containers No. 2 and No. 4 and take to dryness on a hot plate.

5.3.3 Sample Extraction for lead. Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Then transfer the residue from Containers No. 2 and No. 4 to the 125-ml Erlenmeyer flask that contains the filter using rubber policeman and 10 ml of 50 percent HNO_3 for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO_3 whichever is larger.

Place the Erlenmeyer flask on a hot plate and heat with periodic stirring for 30 min at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO_3. Add 10 ml of 3 percent H_2O_2 and continue heating for 10 min. Add 50 ml of hot (80°C) deionized distilled water and heat for 20 min. Remove the flask from the hot plate and allow to cool. Filter the sample through a Millipore membrane filter or equivalent and transfer the filtrate to a 250-ml volumetric flask. Dilute to volume with deionized distilled water.

5.3.4 Filter Blank. Determine a filter blank using two filters from each lot of filters used in the sampling train. Cut each filter into strips and place each filter in a separate 125-ml Erlenmeyer flask. Add 15 ml of 50 percent HNO_3 and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot, deionized distilled water. Filter and dilute to a toal volume of 100 ml using deionized distilled water.

5.3.5 0.1 N HNO_3 Blank. Take the entire 200 ml of 0.1 N HNO_3 to dryness on a steam bath, add 15 ml of 50 percent HNO_3, and treat as described in Section 5.3.3 using 10 ml of 3 percent H_2O_2 and 50 ml of hot, deionized distilled water. Dilute to a total volume of 100 ml using deionized distilled water.

5.4 Analysis.

5.4.1 Lead Determination. Calibrate the spectrophotometer as described in Section 6.2 and determine the absorbance for each source sample, the filter blank, and 0.1 N HNO_3 blank. Analyze each sample three times in this manner. Make appropriate dilutions, as required, to bring all sample Pb concentrations into the linear absorbance range of the spectrophotometer.

If the Pb concentration of a sample is at the low end of the calibration curve and high accuracy is required, the sample can be taken to dryness on a hot plate and the residue dissolved in the appropriate volume of water to bring it into the optimum range of the calibration curve.

5.4.2 Mandatory Check for Matrix Effects on the Lead Results. The analysis for Pb by atomic absorption is sensitive to the chemical compositon and to the physical properties (viscosity, pH) of the sample (matrix effects). Since the Pb procedure described here will be applied to many different sources, many sample matrices will be encountered. Thus, check (mandatory) at least one sample from each source using the Method of Additions to ascertain that the chemical composition and physical properties of the sample did not cause erroneous analytical results.

Three acceptable "Method of Additions" procedures are described in the General Procedure Section of the Perkin Elmer Corporation Manual (see Citation 9.1). If the results of the Method of Additions procedure on the source sample do not agree within 5 percent of the value obtained by the conventional atomic absorption analysis, then the tester must reanalyze all samples from the source using the Method of Additions procedure.

5.4.3 *Container No. 3* (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

6. *Calibration.*

Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Spectrophotometer. Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement (±3 percent) is obtained between two consecutive readings.

Plot the absorbance (y-axis) versus concentration in μg Pb/ml (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than ±0.003 absorbance units, check for incorrectly prepared standards and for curvature in the calibration curve.

To determine stability of the calibration curve, run a blank and a standard after every five samples and recalibrate, as necessary.

7. *Calculations.*

7.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the total volume of dry gas metered corrected to standard conditions (20°C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{m(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

7.2 Volume of Water Vapor and Moisture Content. Using data obtained in this test and Equations 5-2 and 5-3 of Method 5, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas.

7.3 Total Lead in Source Sample. For each source sample correct the average absorbance for the contribution of the filter blank and the 0.1 N HNO_3 blank. Use the calibration curve and this corrected absorbance to determine the μg Pb concentration in the sample aspirated into the spectrophotometer. Calculate the total Pb content C^{*}_{Pb} (in μg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

7.4 Lead Concentration. Calculate the stack gas Pb concentration C_{Pb} in mg/dscm as follows:

$$C_{Pb} = K \frac{C^{*}_{Pb}}{V_{m(std)}}$$

Where:

$K = 0.001$ mg/μg for metric units.
$= 2.205$ lb/μg for English units.

7.5 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively. To calculate v_s, the average stack gas velocity, use Equation 2-9 of Method 2 and the data from this field test.

8. *Alternative Test Methods for Inorganic Lead.*

8.1 Simultaneous Determination of Particulate and Lead Emissions. The tester may use Method 5 to simultaneously determine Pb provided that (1) he uses acetone to remove particulate from the probe and inside of the filter holder as specified by Method 5, (2) he uses 0.1 N HNO_3 in the impingers, (3) he uses a glass fiber filter with a low Pb background, and (4) he treats and analyzes the entire train contents, including the impingers, for Pb as described in Section 5 of this method.

8.2 Filter Location. The tester may use a filter between the third and fourth impinger provided that he includes the filter in the analysis for Pb.

8.3 In-stack Filter. The tester may use an in-stack filter provided that (1) he uses a glass-lined probe and at least two impingers, each containing 100 ml of 0.1 N HNO_3, after the in-stack filter and (2) he recovers and analyzes the probe and impinger contents for Pb. Recover sample from the nozzle with acetone if a particulate analysis is to be made.

9. *Bibliography*

9.1 Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut. September 1976.

9.2 American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. Philadelphia, Pa. 1974. p. 40–42.

9.3 Klein, R. and C. Hach. Standard Additions—Uses and Limitations in Spectrophotometric Analysis. *Amer. Lab.* 9:21-27. 1977.

9.4 Mitchell, W.J. and M.R. Midgett. Determining Inorganic and Alkyl Lead Emissions from Stationary Sources. U.S. Environmental Protection Agency. Emission Monitoring and Support Laboratory. Research Triangle Park, N.C. (Presented at National APCA Meeting. Houston. June 26, 1978).

9.5 Same as Method 5, Citations 2 to 5 and 7 of Section 7.

PROPOSED RULE DECEMBER 12, 1983

1. By revising Section 5.4.2 to read as follows:

5.4.2 Check for Matrix Effects on the Lead Results. Since the analysis for Pb by atomic absorption is sensitive to the chemical composition and to the physical properties (viscosity, pH) of the sample (matrix effects), the analyst shall check at least one sample from each source using the method of additions as follows:

Add or spike an equal volume of standard solution to an aliquot of the sample solution, then measure the absorbance of the resulting solution and the absorbance of an aliquot of unspiked sample.

Next, calculate the Pb concentration C_s in µg/ml of the sample solution by using the following equation:

$$C_s = C_a \frac{A_s}{A_t - A_s} \qquad \text{Eq. 12–1}$$

Where:

C_a=Pb concentration of the standard solution, µg/ml.

A_s=Absorbance of the sample solution.

A_t=Absorbance of the spiked sample solution.

Volume corrections will not be required if the solutions as analyzed have been made to the same final volume. Therefore, C_s and C_a represent lead concentration before dilutions.

Method of additions procedures described on pages 9–4 and 9–5 of the section entitled "General Information" of the Perkin Elmer Corporation Atomic Absorption Spectrophotometry Manual, Number 303–0152 (see Section 9.1) may also be used. In any event, if the results of the method of additions procedure used on the source sample do not agree to within 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using a method of additions procedure.

2. By correcting the symbol "$V_{m(std)}$" to "$V_{w(std)}$" in Section 7.2, line 3.

3. By adding "Eq. 12–2" to the right of the equation in Section 7.4.

4. By inserting "$\times 10^{-9}$" immediately after the number "2.205" in the last line of Section 7.4

METHOD 13B—DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES—SPECIFIC ION ELECTRODE METHOD

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the specific ion electrode method.

2. Range and Sensitivity

The range of this method is 0.02 to 2,000 μg F/ml; however, measurements of less than 0.1 μg F/ml require extra care. Sensitivity has not been determined.

3. Interferences

Grease on sample-exposed surfaces may cause low F results because of adsorption.

4. Precision and Accuracy

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a of 12 samples per sampling run. Fluoncentrations encountered during the anged from 0.1 to 1.4 mg F/m^3. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F/m^3 with 60 degrees of freedom and 0.056 mg F/m^3 with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

5. Apparatus

5.1 Sampling Train and Sample Recovery. Same as Method 13A, Sections 5.1 and 5.2, respectively.

5.2 Analysis. The following items are needed:

5.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 5.3.1 to 5.3.9, respectively, except include also 100-ml polyethylene beakers.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode. Single junction, sleeve type.

5.2.4 Electrometer. A pH meter with millivolt-scale capable of ±0.1-mv resolution, or a specific ion meter made specifically for specific ion use.

5.2.5 Magnetic Stirrer and TFE[1] Fluorocarbon-Coated Stirring Bars.

6. Reagents

1 Sampling and Sample Recovery. as Method 13A, Sections 6.1 and 6.2, tively.

Analysis. Use ACS reagent grade emicals (or equivalent), unless otherwise specified. The reagents needed for analysis are as follows:

6.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.2.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml deionized distilled water.

6.2.3 Sodium Hydroxide (NaOH). Pellets.

6.2.4 Sulfuric Acid (H_2SO_4), Concentrated.

6.2.5 Filters. Whatman No. 541, or equivalent.

6.2.6 Water. From same container as 6.1.2 of Method 13A.

6.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of deionized distilled water.

6.2.8 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

6.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of deionized distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-liter volumetric flask, and dilute to volume with deionized distilled water. Commercially prepared TISAB may be substituted for the above.

6.2.10 Fluoride Standard Solution, 0.1 M. Oven dry some sodium fluoride (NaF) for a minimum of 2 hours at 110°C, and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough deionized distilled water to dissolve. Dilute to volume with deionized distilled water.

7. Procedure

7.1 Sampling, Sample Recovery, and Sample Preparation and Distillation. Same as Method 13A, Sections 7.1, 7.2, and 7.3, respectively, except the notes concerning chloride and sulfate interferences are not applicable.

7.2 Analysis.

7.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ±2°C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material such as cork, between the stirrer and the beaker. Hold dilute samples (below 10^{-4} M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with deionized distilled water.

7.2.2 Container No. 3 (Silica Gel). Same as Method 13A, Section 7.4.2.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Same as Method 13A.

8.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with deionized distilled water for a 10^{-2} M standard solution. Use 10 ml of 10^{-2} M solution to make a 10^{-3} M solution in the same manner. Repeat the dilution procedure and make 10^{-4} and 10^{-5} solutions.

Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of 10^{-2} M standard is diluted with 50 ml of TISAB, the concentration is still designated "10^{-2} M."

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10^{-5} and 10^{-4} M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10^{-2} M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

(NOTE: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.)

9. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

9.1 Nomenclature. Same as Method 13A, Section 9.1. In addition:

M = F concentration from calibration curve, molarity.

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation and Acceptable Results. Same as Method 13A, Section 9.2 to 9.4, 9.5.2, and 9.6, respectively.

9.3 Fluoride in Sample. Calculate the amount of F in the sample using the following:

$$F_t = K \frac{V_t}{A_t} V_d \; M \qquad \text{Equation 13B-1}$$

Where:

K = 19 mg/millimole

10. *References*

1. Same as Method 13A, Citations 1 and 2 of Section 10.

2. MacLeod, Kathryn E. and Howard L. Crist. Comparison of the SPADNS—Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. Analytical Chemistry. 45:1272-1273. 1973.

METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. *Definitions.*

2.1 Measurement System. The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.4 Zero Drift. The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift. The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 Response Time. The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3. *Apparatus.*

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

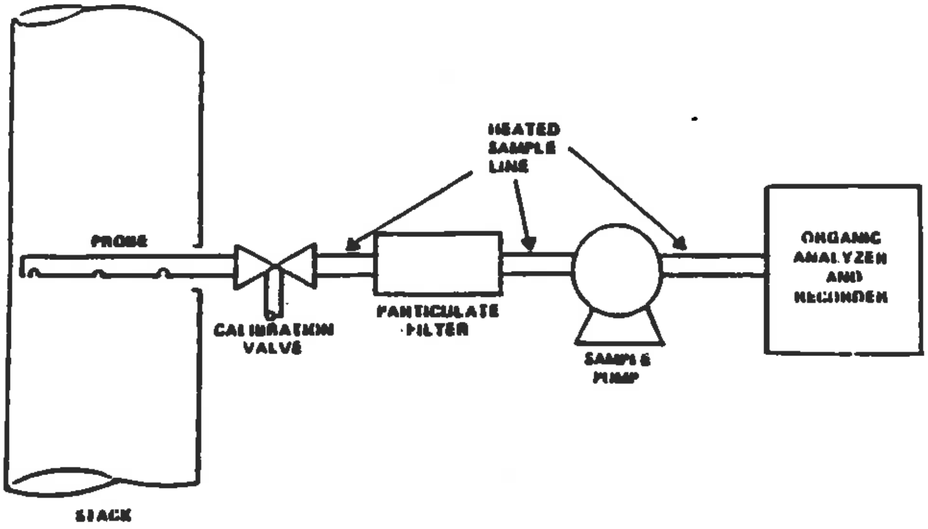

Figure 25A-1. Organic Concentration Measurement System.

3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon® tubing to transport the sample gas to the analyzers. The sample line should be heated, if necessary, to prevent condensation in the line.

3.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4. *Calibration and Other Gases.*

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

4.1 Fuel. A 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5. *Measurement System Performance Specifications.*

5.1 Zero Drift. Less than ±3 percent of the span value.

5.2 Calibration Drift. Less than ±3 percent of span value.

5.3 Calibration Error. Less than ±5 percent of the calibration gas value.

6. *Pretest Preparations.*

6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters (whichever is less) upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (>1.0 percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7. *Emission Measurement Test*

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8. *Organic Concentration Calculations.*

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K\, C_{meas}$$

Eq. 25A-1

Where:

C_c = Organic concentration as carbon, ppmv.

C_{meas} = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor.

- K = 2 for ethane.
- K = 3 for propane.
- K = 4 for butane.
- K = Appropriate response factor for other organic calibration gases.

9. *Bibliography.*

9.1 Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, N.C. June 1978.

9.3 Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N.C. EMB Report No. 75-GAS-6. August 1975.

METHOD 101A—DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM SEWAGE SLUDGE INCINERATORS

INTRODUCTION

This method is similar to Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for collection.

1. *Applicability and Principle*—1.1 *Applicability.* This method applies to the determination of particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations.

1.2 *Principle.* Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and Sensitivity*—2.1 *Range.* After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 *Sensitivity.* The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents*—3.1 *Sampling.* Excessive oxidizable organic matter in the stack gas prematurely depletes the $KMnO_4$ solution and thereby prevents further collection of Hg.

3.2 *Analysis.* Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision*—Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 μg Hg/ml in the concentration range of 50 to 130 μg Hg/m^3.

5. *Apparatus*—5.1 *Sampling Train and Sample Recovery.* Same as Method 101, Sections 5.1 and 5.2, respectively, except for the following variations:

5.1.1 *Probe Liner.* Same as Method 101, Section 5.1.2, except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 *Filter Holder (Optional).* Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber of Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 14°C (248 ± 25° F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 *Analysis.* The apparatus needed for analysis is the same as Method 101, Sections 5.3 and 5.4, except as follows:

5.2.1 *Volumetric Pipets.* Class A; 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

5.2.2 *Graduated Cylinder.* 25-ml.

5.2.3 *Steam Bath.*

6. *Reagents—Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.*

6.1 *Sampling and Recovery.* The reagents used in sampling and recovery are as follows:

6.1.1 *Water.* Deionized distilled, meeting ASTM Specifications for Type I Reagent Water—ASTM Test Method D1193-77 (incorporated by reference—see § 61.18). If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 *Nitric Acid (HNO_3), 50 Percent (V/V).* Mix equal volumes of concentrated HNO_3 and deionized distilled water, being careful to slowly add the acid to the water.

6.1.3 *Silica Gel.* Indicating type, 6- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hr. The tester may use new silica gel as received.

6.1.4 *Filter (Optional).* Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 μm dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.

6.1.5 *Sulfuric Acid (H_2SO_4), 10 Percent (V/V).* Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.

6.1.6 *Absorbing Solution, 4 Percent $KMnO_4$ (W/V).* Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

6.2 *Analysis.* The reagents needed for analysis are listed below:

6.2.1 *Tin (II) Solution.* Prepare fresh daily and keep sealed when not being used. Competely dissolve 20 g of tin (II) chloride [or 25 g of tin (II) sulfate] crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 *Sodium Chloride—Hydroxylamine Solution.* Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in deionized distilled water and dilute to 100 ml.

6.2.3 *Hydrochloric Acid (HCl), 8 N.* Dilute 67 ml of concentrated HNO_3 to 100 ml with deionzed distilled water (slowly add the HCl to the water).

6.2.4 *Nitric Acid, 15 Percent (V/V).* Dilute 15 ml of concentrated HNO_3 to 100 ml with deionized distilled water.

6.2.5 *Mercury Stock Solution, 1 mg Hg/ml.* Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of deionized distilled water. Add 100 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 *Intermediate Mercury Standard Solution, 10 μg Hg/ml.* Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (Section 6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO_3 solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.7 *Working Mercury Standard Solution, 200 ng Hg/ml.* Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (Section 6.2.6) into a 250-ml volumetric flask. Add 5 ml of 4 percent $KMnO_4$ absorbing solution and 5 ml of 15 percent HNO_3. Adjust the volume to exactly 250 ml with deionized distilled water. Mix thoroughly.

6.2.8 *Potassium Permanganate, 5 Percent (W/V).* Dissolve 5 g of $KMnO_4$ in deionized distilled water and dilute to 100 ml.

6.2.9 *Filter.* Whatman No. 40 or equivalent.

7. *Procedure*—7.1 *Sampling.* The sampling procedure is the same as Method 101, except for changes due to the use of $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 *Preliminary Determinations.* The preliminary determinations are the same as those given in Method 101, Section 7.1.2, except for the absorbing solution depletion sign. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted. In cases where an excess of water condensation is encountered, collect two runs to make one sample.

7.1.2 *Preparation of Sampling Train.* The preparation of the sampling train is the same as that given in Method 101, Section 7.1.3, except for the cleaning of the glassware [probe, filter holder (if used), impingers, and connectors] and the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 ml of 4 percent $KMnO_4$ in the first impinger and 100 ml in each of the second and third impingers.

If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter and place the gasket in proper position to prevent the sample gas stream from by-passing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3 *Sampling Train Operation.* In addition to the procedure given in Method 101, Section 7.1.5, maintain a temperature around the filter (if applicable) of 120°±14° C (248°±25° F).

7.2 *Sample Recovery.* Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid out from the impingers.

Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe, impinger assembly, and (if applicable) filter assembly to a clean-up area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger, Probe, and Filter Holder). Use a graduated cylinder; measure the liquid in the first three impingers to within ±1 ml. Record the volume of liquid present (e.g., see Figure 5-3 of Method 5 in Part 60 of 40 CFR). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 7.1.2.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

NOTE: If a filter is used, remove the filter from its holder, as outlined under "Container No. 3" below.)

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner and front half of the filter holder (if applicable) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent $KMnO_4$ solution; add all washings to the 1000-ml glass sample bottle; remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required; and add this HCl rinse to this sample container.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

7.2.2. *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7.2.3 *Container No. 3* (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of 4 percent $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

7.2.4 *Container No. 4* (Filter Blank). If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 *Container No. 5* (Absorbing Solution Blank). For a blank, place 500 ml of 4 percent $KMnO_4$ absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 *Sample Preparation*. Check liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below.

7.3.1 *Containers No. 3 and No. 4* (Filter and Filter Blank). If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70° C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 *Container No. 1* (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman 40 filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4 percent $KMnO_4$ absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.3.3 *Container No. 5* (Absorbing Solution Blank). Treat this container as described in Section 7.3.2. Combine this filtrate with the filtrate with Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 *Analysis*. Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 and 8.2 Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within ±3 percent of their average value. If the 10-ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

8. *Calibration and Standards*—The calibration and standards are the same as Method 101, Section 8, except for the following variations:

8.1 *Optical Cell Heating System Calibration*. Same as method 101, Section 8.2, except use a 25-ml graduated cylinder to add 25 ml of deionized distilled water to the bottle section of the aeration cell.

8.2 *Spectrophotometer and Recorder Calibration*. The mercury response may be measured by either peak height or peak area. (NOTE: the temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.) Set the spectrophotometer wave length at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation.

Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell. (NOTE: Always add the Hg-containing solution to the aeration cell after the 25 ml of deionized distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent $KMnO_4$ absorbing solution followed by 5 ml of 15 percent HNO_3 and 5 ml of 5 percent $KMnO_4$ to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride hydroxylamine in 1-ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

9. *Calculations*—9.1 *Dry Gas Volume, Volume of Water Vapor and Moisture Content, Stack Gas Velocity, Isokinetic Variation and Acceptable Results, and Determination of Compliance.* Same as Method 101, Sections 9.1, 9.2, 9.3, 9.6, and 9.7, respectively, except use data obtained from this test.

9.2 *Total Mercury*. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within ±3 percent of their average for the contribution of the field blank. Then calculate the total Hg content in µg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 *Mercury Emission Rate*. Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-1. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = K \frac{m_{Hg} v_s A_s (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}](T_s/P_s)}$$

Eq. 101A-1

Where:

m_{Hg} = Total Hg content in each sample, µg.
v_s = Average stack gas velocity, m/sec (fps).
A_s = Stack cross-sectional area, m^2 (ft^2).
86,400 = Conversion factor, sec/day.
10^{-6} = Conversion factor, g/µg.
$V_{m(std)}$ = Dry gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).

$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).
T_s = Absolute average stack gas temperature, °K (°R).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
K = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

10. *Bibliography*. 1. Same as Method 101, Section 10.

2. Mitchell, W. J., M. R. Midgett, J. C. Suggs, and D. Albrinck.

Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. Publication No. EPA-600/4-79-058. September 1979.

METHOD 101A—DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM SEWAGE SLUDGE INCINERATORS

INTRODUCTION

This method is similar to Method 101, except acidic potassium permangante solution is used instead of acidic iodine monochloride for collection.

1. *Applicability and Principle*—1.1 *Applicability.* This method applies to the determination of particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations.

1.2 *Principle.* Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and Sensitivity*—2.1 *Range.* After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 *Sensitivity.* The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents*—3.1 *Sampling.* Excessive oxidizable organic matter in the stack gas prematurely depletes the $KMnO_4$ solution and thereby prevents further collection of Hg.

3.2 *Analysis.* Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision*—Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 μg Hg/ml in the concentration range of 50 to 130 μg Hg/m^3.

5. *Apparatus*—5.1 *Sampling Train and Sample Recovery.* Same as Method 101, Sections 5.1 and 5.2, respectively, except for the following variations:

5.1.1 *Probe Liner.* Same as Method 101, Section 5.1.2, except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 *Filter Holder (Optional).* Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber of Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 14°C (248 ± 25° F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 *Analysis.* The apparatus needed for analysis is the same as Method 101, Sections 5.3 and 5.4, except as follows:

5.2.1 *Volumetric Pipets.* Class A; 1-, 2-, 3-4-, 5-, 10-, and 20-ml.

5.2.2 *Graduated Cylinder.* 25-ml.

5.2.3 *Steam Bath.*

6. *Reagents—Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.*

6.1 *Sampling and Recovery.* The reagents used in sampling and recovery are as follows:

6.1.1 *Water.* Deionized distilled, meeting ASTM Specifications for Type I Reagent Water—ASTM Test Method D1193-77 (incorporated by reference—see § 61.18). If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 *Nitric Acid (HNO_3), 50 Percent (V/V).* Mix equal volumes of concentrated HNO_3 and deionized distilled water, being careful to slowly add the acid to the water.

6.1.3 *Silica Gel.* Indicating type, 6- to 16-mesh. If previously used, dry at 175° C (350° F) for 2 hr. The tester may use new silica gel as received.

6.1.4 *Filter (Optional).* Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 μm dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.

6.1.5 *Sulfuric Acid (H_2SO_4), 10 Percent (V/V).* Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.

6.1.6 *Absorbing Solution, 4 Percent $KMnO_4$ (W/V).* Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

6.2 *Analysis.* The reagents needed for analysis are listed below:

6.2.1 *Tin (II) Solution.* Prepare fresh daily and keep sealed when not being used. Competely dissolve 20 g of tin (II) chloride [or 25 g of tin (II) sulfate] crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 *Sodium Chloride—Hydroxylamine Solution.* Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in deionized distilled water and dilute to 100 ml.

6.2.3 *Hydrochloric Acid (HCl), 8 N.* Dilute 67 ml of concentrated HNO_3 to 100 ml with deionzed distilled water (slowly add the HCl to the water).

6.2.4 *Nitric Acid, 15 Percent (V/V).* Dilute 15 ml of concentrated HNO_3 to 100 ml with deionized distilled water.

6.2.5 *Mercury Stock Solution, 1 mg Hg/ml.* Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of deionized distilled water. Add 100 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 *Intermediate Mercury Standard Solution, 10 μg Hg/ml.* Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (Section 6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO_3 solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.7 *Working Mercury Standard Solution, 200 ng Hg/ml.* Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (Section 6.2.6) into a 250-ml volumetric flask. Add 5 ml of 4 percent $KMnO_4$ absorbing solution and 5 ml of 15 percent HNO_3. Adjust the volume to exactly 250 ml with deionized distilled water. Mix thoroughly.

6.2.8 *Potassium Permanganate, 5 Percent (W/V).* Dissolve 5 g of $KMnO_4$ in deionized distilled water and dilute to 100 ml.

6.2.9 *Filter.* Whatman No. 40 or equivalent.

7. *Procedure*—7.1 *Sampling.* The sampling procedure is the same as Method 101, except for changes due to the use of $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 *Preliminary Determinations.* The preliminary determinations are the same as those given in Method 101, Section 7.1.2, except for the absorbing solution depletion sign. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted. In cases where an excess of water condensation is encountered, collect two runs to make one sample.

7.1.2 *Preparation of Sampling Train.* The preparation of the sampling train is the same as that given in Method 101, Section 7.1.3, except for the cleaning of the glassware [probe, filter holder (if used), impingers, and connectors] and the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 ml of 4 percent $KMnO_4$ in the first impinger and 100 ml in each of the second and third impingers.

If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter and place the gasket in proper position to prevent the sample gas stream from by-passing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3 *Sampling Train Operation.* In addition to the procedure given in Method 101, Section 7.1.5, maintain a temperature around the filter (if applicable) of 120°±14° C (248°±25° F).

7.2 *Sample Recovery.* Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid out from the impingers.

Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe, impinger assembly, and (if applicable) filter assembly to a clean-up area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger, Probe, and Filter Holder). Use a graduated cylinder; measure the liquid in the first three impingers to within ±1 ml. Record the volume of liquid present (e.g., see Figure 5-3 of Method 5 in Part 60 of 40 CFR). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 7.1.2.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

NOTE: If a filter is used, remove the filter from its holder, as outlined under "Container No. 3" below.)

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner and front half of the filter holder (if applicable) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent $KMnO_4$ solution; add all washings to the 1000-ml glass sample bottle; remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required; and add this HCl rinse to this sample container.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

7.2.2. *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7.2.3 *Container No. 3* (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of 4 percent $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

7.2.4 *Container No. 4* (Filter Blank). If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 *Container No. 5* (Absorbing Solution Blank). For a blank, place 500 ml of 4 percent $KMnO_4$ absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 *Sample Preparation*. Check liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below.

7.3.1 *Containers No. 3 and No. 4* (Filter and Filter Blank). If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70° C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 *Container No. 1* (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman 40 filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4 percent $KMnO_4$ absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.3.3 *Container No. 5* (Absorbing Solution Blank). Treat this container as described in Section 7.3.2. Combine this filtrate with the filtrate with Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 *Analysis*. Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 and 8.2 Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within ±3 percent of their average value. If the 10-ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

8. *Calibration and Standards*—The calibration and standards are the same as Method 101, Section 8, except for the following variations:

8.1 *Optical Cell Heating System Calibration*. Same as method 101, Section 8.2, except use a 25-ml graduated cylinder to add 25 ml of deionized distilled water to the bottle section of the aeration cell.

8.2 *Spectrophotometer and Recorder Calibration*. The mercury response may be measured by either peak height or peak area. (NOTE: the temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.) Set the spectrophotometer wave length at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation.

Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell. (NOTE: Always add the Hg-containing solution to the aeration cell after the 25 ml of deionized distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent $KMnO_4$ absorbing solution followed by 5 ml of 15 percent HNO_3 and 5 ml of 5 percent $KMnO_4$ to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride hydroxylamine in 1-ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

9. *Calculations*—9.1 *Dry Gas Volume, Volume of Water Vapor and Moisture Content, Stack Gas Velocity, Isokinetic Variation and Acceptable Results, and Determination of Compliance*. Same as Method 101, Sections 9.1, 9.2, 9.3, 9.6, and 9.7, respectively, except use data obtained from this test.

9.2 *Total Mercury*. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within ±3 percent of their average for the contribution of the field blank. Then calculate the total Hg content in µg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 *Mercury Emission Rate*. Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-1. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = K \frac{m_{Hg} v_s A_s (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}](T_s/P_s)}$$

Eq. 101A-1

Where:

m_{Hg} = Total Hg content in each sample, µg.
v_s = Average stack gas velocity, m/sec (fps).
A_s = Stack cross-sectional area, m^2 (ft^2).
86,400 = Conversion factor, sec/day.
10^{-6} = Conversion factor, g/µg.
$V_{m(std)}$ = Dry gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).

$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).
T_s = Absolute average stack gas temperature, °K (°R).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
K = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

10. *Bibliography*. 1. Same as Method 101, Section 10.

2. Mitchell, W. J., M. R. Midgett, J. C. Suggs, and D. Albrinck.

Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. Publication No. EPA-600/4-79-058. September 1979.

Method 104—Reference Method for Determination of Beryllium Emissions From Stationary Sources

1. *Applicability and Principle.*

1.1 Applicability. This method is applicable for the determination of beryllium (Be) emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

1.2 Principle. Be emissions are isokinetically sampled from the source, and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry.

2. *Apparatus.*

2.1 Sampling Train. The sampling train is identical to the Method 5 train as shown in Figure 5-1 (mention of Method 5 refers to 40 CFR Part 60). The sampling train consists of the following components:

2.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.8, 2.1.9, and 2.1.10, respectively.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing. The tester may use a heating system capable of maintaining a gas temperature of 120±14°C (248±25°F) at the probe exit during sampling to prevent water condensation. *Note:* Do not use metal probe liners.

2.1.3 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to the approval of the Administrator. (*Note:* Mention of trade names of specific products does not constitute endorsement by the Environmental Protection Agency.) The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

2.1.4 Impingers. Four Greenburg-Smith impingers connnected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, the tester may use impingers that are modified by replacing the tip with a 13-mm-ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask.

2.2 Sample Recovery. The following items are needed:

2.2.1 Probe Cleaning Rod. At least as long as probe.

2.2.2 Glass Sample Bottles. Leakless, with Teflon-lined caps, 500-ml.

2.2.3 Graduated Cylinder. 250-ml.

2.2.4 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.5 Funnel. Glass, to aid in sample recovery.

2.2.6 Plastic Jar. Approximately 300-ml.

2.3 Analysis. The following equipment is needed:

2.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, with nitrous oxide/acetylene burner.

2.3.2 Hot Plate.

2.3.3 Perchloric Acid Fume Hood.

3. *Reagents.*

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

3.1 Sampling and Recovery. The reagents used in sampling and recovery are as follows:

3.1.1 Filter. Millipore AA, or equivalent. It is suggested that a Whatman 41 filter or equivalent be placed immediately against the back side of the Millipore filter as a guard against breaking the Millipore filter. To be equivalent, other filters shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency tests shall be conducted in accordance with ASTM Standard Method D 2986-71 (reapproved 1978) (incorporated by reference—see § 61.18). Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Water. Deionized distilled, meeting ASTM Specifications for Type 3 Reagent Water—ASTM Test Method D 1193-77 (incorporated by reference—see § 61.18). If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter.

3.1.3 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175°C (350°F) for 2 hours. The tester may use new silica gel as received.

3.1.4 Acetone.

3.1.5 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl).

Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

3.2 Sample Preparation and Analysis. The reagents needed are listed below:

3.2.1 Water. Same as Section 3.1.2.

3.2.2. Perchloric Acid ($HClO_4$). Concentrated (70 percent).

3.2.3 Nitric Acid (HNO_3). Concentrated.

3.2.4 Beryllium Powder. Minimum purity 98 percent.

3.2.5 Sulfuric Acid (H_2SO_4) Solution, 12 N. Dilute 33 ml of concentrated H_2SO_4 to 1 liter with water.

3.2.6 Hydrochloric Acid Solution, 25 percent HCl (V/V).

3.2.7 Standard Beryllium Solution, 1 μg Be/ml. Dissolve 10 mg of Be in 80 ml of 12NH_2SO_4 solution, and dilute to 1000 ml with water. Dilute a 10-ml aliquot to 100 ml with 25 percent HCl solution to give a concentration of 1 μg/ml. Prepare this dilute stock solution fresh daily. Equivalent strength Be stock solutions may be prepared from Be salts such as $BeCl_2$ and $Be(NO_3)_2$ (98 percent minimum purity).

4. *Procedure.*

4.1 Sampling. Because of the complexity of this method testers should be trained and experienced with the test procedures to assure reliable results. As Be is hazardous, testers should take precautions to minimize exposure. The amount of Be that is collected is generally small, therefore, it is necessary to exercise particular care to prevent contamination or loss of sample.

4.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 4.1.1. Omit the directions of filters, except check them visually against light for irregularities and flaws such as pinholes.

4.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 4.1.2, except as follows: Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

Obtain samples over a period or periods of time that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours per run is recommended.

4.1.3 Prior to assembly, clean all glassware (probe, impingers, and connectors) by first soaking in wash acid for 2 hours, followed by rinsing with water. Place 100 ml of water in each of the first two impingers, and leave the third impinger empty. Save a portion of the water for a blank analysis. Place approximately 200 g of preweighted silica gel in the fourth impinger. The tester may use more silica gel, but should be careful to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. As an alternative, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g.

Install the selected nozzel using a Viton A O-ring when stack temperatures are less the 260°C (500°F). Use a fiberglass string gasket if temperatures are higher. See APTD-0576 (Citation 9 in Section 10 of Method 101) for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used.

If condensation in the probe or filter is a problem, probe and filter heaters will be required. Adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 225°F. If the stack gas is in excess of about 200°F, consideration should be given to an alternate procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as shown in Figure 5-1 of Method 5, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicon grease. *Note:* An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

After the sampling train has been assembled, turn on and set the probe, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

4.1.4. Leak-Check Procedures. Follow the leak-check procedures outlined in Method 5, Sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak Checks During Sample Run), and 4.1.4.3 (Post-Test Leak Check).

4.1.5 Beryllium Train Operation. Follow the general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

4.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

4.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle, and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling. Capping would create a vacuum and draw liquid out from the impingers.

Before moving the sampling train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Be contamination.

Inspect the train before and during this assembly, and note any abnormal conditions. Treat the sample as follows:

Disconnect the probe from the impinger train. Remove the filter and any loose particulate matter from the filter holder, and place in a sample bottle. Place the contents (measured to ±1 ml) of the first three impingers into another sample bottle. Rinse the probe and all glassware between it and the back half of the third impinger with water and acetone, and add this to the latter sample bottle. Clean the probe with a brush or a long slender rod and cotton balls. Use acetone while cleaning. Add these to the sample bottle. Retain a sample of the water and acetone as a blank. The total amount of water and acetone used should be measured for accurate blank correction. Place the silica gel in the plastic jar. Seal and secure all sample containers for shipment. If an additional test is desired, the glassware can be carefully double rinsed with water and reassembled. However, if the glassware is out of use more than 2 days, repeat the initial acid wash procedure.

4.3 Analysis.

4.3.1 Apparatus Preparation. Before use, clean all glassware according to the procedure of Section 4.1.3. Adjust the instrument settings according to the instrument manual, using an absorption wavelength of 234.8 nm.

4.3.2 Sample Preparation. The digestion of Be samples is accomplished in part in concentrated $HClO_4$. *Caution:* The analyst must insure that the sample is heated to light brown fumes after the initial HNO_3 addition; otherwise, dangerous perchlorates may result from the subsequent $HClO_4$ digestion. $HClO_4$ should be used only under a hood.

4.3.2.1 Filter Preparation. Transfer the filter and any loose particulate matter from the sample container to a 150-ml beaker. Add 35 ml concentrated HNO_3. Heat on a hotplate until light brown fumes are evident to destroy all organic matter. Cool to room temperature, and add 5 ml concentrated H_2SO_4 and 5 ml concentrated $HClO_4$. Then proceed with step 4.3.2.4.

4.3.2.2 Water Preparation. Place a portion of the water and acetone sample into a 150-ml beaker, and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness. Cool the residue, and add 35 ml concentrated HNO_3. Heat on a hotplate until light brown fumes are evident to destroy any organic matter. Cool to room temperature, and add 5 ml concentrated H_2SO_4 and 5 ml concentrated $HClO_4$. Then proceed with step 4.3.2.4.

4.3.2.3 Silica Gel Preparation Analyses. Weigh the spent silica gel, and report to the nearest gram.

4.3.2.4 Final Sample Preparation. Samples from 4.3.2.1 and 4.3.2.2 may be combined here for ease of analysis. Replace on a hotplate, and evaporate to dryness in a $HClO_4$ hood. Cool and dissolve the residue in 10.0 ml of 25 percent V/V HCl. Samples are now ready for the atomic absorption unit. It is necessary for the Be concentration of the sample to be within the calibration range of the unit. If necessary, perform further dilution of sample with 25 percent V/V HCl to bring the sample within the calibration range.

4.3.3 Beryllium Determination. Analyze the samples prepared in 4.3.2 at 234.8 nm using a nitrous oxide/acetylene flame. Aluminum, silicon and other elements can interfere with this method if present in large quantities. Standard methods are available, however, that may be used to effectively eliminate these interferences (see Citation 2 in Section 8).

5. *Calibration.*

5.1 Sampling Train. Calibrate the sampling train components according to the procedures outlined in the following sections of Method 5: Section 5.1 (Probe Nozzle), Section 5.2 (Pitot Tube), Section 5.3 (Metering System), Section 5.4 (Probe Heater), Section 5.5 (Temperature Gauges), Section 5.7 (Barometer). Note that the leak check described in Section 5.6 of Method 5 applies to this method.

6. *Calculations.*

6.1 Dry Gas Volume. Using the data from each sample run, calculate the dry gas sample volume at standard conditions $V_{m(std)}$ (corrected for leakage, if necessary) as outlined in Section 6.3 of Method 5.

6.2 Volume of Water Vapor in Sample and Moisture Content of Stack Gas. Using the data obtained from each sample run, calculate the volume of water vapor $V_{w(std)}$ in the sample, and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

6.3 Stack Gas Velocity. Using the data from each sample run and Equation 2-9 of Method 2, calculate the average stack gas velocity $v_{s(avg)}$.

6.4 Beryllium Emission Rate. Calculate the Be emission rate R in g/day for each stack using Equation 104-1. For cyclic operations, use only the time per day each stack is in operation. The total Be emission rate from a source will be the summation of results from all stacks.

Eq. 104-1

$$R = K \frac{W_t v_{s(avg)} A_s (86{,}400 \times 10^{-6})}{(V_{m(std)} + V_{w(std)})(T_s/P_s)}$$

Where:

W_t = Total weight of Be collected, µg.
A_s = Stack cross-sectional area, M^2 (ft^2).
86,400 = Conversion factor, sec/day.
10^{-6} = Conversion factor, g/µg.
T_s = Absolute average stack gas temperature, °K (°R).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
K = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

6.5 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

7. *Determination of Compliance.* Each performance test consists of three sample runs of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all sample runs.

8. *Bibliography.*

In addition to Citations 1-3 and 5-15 of Section 10 of Method 101, the following citations may be helpful:

1. Amos, M.D., and J. B. Willis. Use of High-Temperature Pre-Mixed Flames in Atomic Absorption Spectroscopy. Spectrochim. Acta. *22*:1325. 1966.

2. Fleet, B., K. V. Liberty, and T. S. West. A Study of Some Matrix Effects in the Determination of Beryllium by Atomic Absorption Spectroscopy in the Nitrous Oxide-Acetylene Flame. Talanta *17*:203. 1970.

APPENDIX B

SAMPLE EXAMPLE CALCULATIONS

EXAMPLE TEST CALCULATIONS

UNIT NO. 1 SDA INLET

RUN NUMBER: I-M26-1

VOLUME OF DRY GAS SAMPLED AT STANDARD CONDITIONS

$$Vm(std) = 17.64 * Y * Vm * \frac{(Pbar + Delta\ H/13.6)}{(460 + tm)}$$

$$Vm(std) = 17.64 * 1.0114 * 117.510 * \frac{(29.5 + 2.52/13.6)}{(460 + 66)} = 118.318\ DSL$$

DRY VOLUMETRIC FLOW RATE AT STANDARD CONDITIONS, CUBIC METERS PER MINUTE

$$Qmsd = Qsd * 0.02832$$

$$Qmsd = 99{,}570 * 0.02832 = 2{,}820$$

CONCENTRATION, HYDROGEN CHLORIDE, MG/DSCM

$$mg/DSCM = \frac{mg}{Vmstd * 0.03531 * 0.02832}$$

$$mg/DSCM = \frac{51.3}{118.318 * 0.03531 * 0.02832} = 434\ mg/DSCM$$

CONCENTRATION, HYDROGEN CHLORIDE, MG/DSCM AT 12% CO2

$$mg/DSCM@12\% = \frac{12}{\%CO2} * mg/DSCM$$

$$mg/DSCM@12\% = \frac{12}{10.0} * 434 = 520\ mg/DSCM\ @\ 12\%\ CO2$$

CONCENTRATION, HYDROGEN CHLORIDE, MG/DSCM AT 7% O2

$$mg/DSCM@7\% = \frac{21 - 7}{21 - \%O2} * mg/DSCM$$

$$mg/DSCM@7\% = \frac{21 - 7}{21 - 9.8} * 434 = 542\ mg/DSCM\ @\ 7\%\ O2$$

CONCENTRATION, HYDROGEN CHLORIDE, PPMVD

$$\text{ppmvd} = \frac{24.056 * \text{mg}/10^3}{\text{Vmstd} * \text{fwt}} * 10^6$$

$$\text{ppmvd} = \frac{24.056 * 51.3/10^3}{118.318 * 36.46} * 10^6 = 286 \text{ ppmd}$$

CONCENTRATION, HYDROGEN CHLORIDE, PPMVD AT 12% CO2

$$\text{ppmvd@12\%} = \frac{12}{\%\text{CO2}} * \text{ppmvd}$$

$$\text{ppmvd@12\%} = \frac{12}{10.0} * 286 = 343 \text{ ppmvd @ 12\% CO2}$$

CONCENTRATION, HYDROGEN CHLORIDE, PPMVD AT 7% O2

$$\text{ppmvd@7\%} = \frac{21 - 7}{21 - \%\text{O2}} * \text{ppmvd}$$

$$\text{ppmvd@7\%} = \frac{21 - 7}{21 - 9.8} * 286 = 358 \text{ ppmvd @ 7\% O2}$$

EMISSION RATE, HYDROGEN CHLORIDE, LB/HR

$$\text{lb/hr} = \frac{60 * \text{mg}/10^3 * \text{Qsd}}{453.592 * (\text{Vmstd} * .03531)}$$

$$\text{lb/hr} = \frac{60 * 51.3/10^3 * 99{,}570}{453.592 * (118.318 * 0.03531)} = 162 \text{ lb/hr}$$

EMISSION RATE, HYDROGEN CHLORIDE, LB/MMBTU

$$\text{lb}/10^6\text{Btu} = \frac{\text{lbs}}{\text{DSCF}} \times \frac{\text{Fd DSCF at 12\% CO}_2}{\text{MMBtu}}$$

EXAMPLE TEST CALCULATIONS RUN O-M5&MMTL-1

Unit No. 1 ESP Outlet

VOLUME OF DRY GAS SAMPLED AT STANDARD CONDITIONS

$$\text{Vmstd} = 17.64 * \text{Y} * \text{Vm} * \frac{\text{Pbar} + (\text{Delta H}/13.6)}{(460 + \text{tm})}$$

$$\text{Vmstd} = 17.64 * 1.0011 * 111.545 * \frac{29.40 + (2.560/13.6)}{(460 + 64)} = 111.228 \text{ DSCF}$$

VOLUME OF WATER VAPOR AT STANDARD CONDITIONS

$$\text{Vwstd} = 0.04707 * \text{Vlc}$$

$$\text{Vwstd} = 0.04707 * 535.0 = 25.182 \text{ SCF}$$

PERCENT MOISTURE, BY VOLUME, AS MEASURED IN FLUE GAS

$$\%H_2O = 100 * \text{Vwstd} / (\text{Vwstd} + \text{Vmstd})$$

$$\%H_2O = \frac{25.182}{25.182 + 111.228} * 100 = 18.5\ \%$$

ABSOLUTE FLUE GAS PRESSURE

$$\text{Ps} = \text{Pbar} + (\text{Pg} / 13.6)$$

$$\text{Ps} = 29.40 + (-4.80/13.6) = 29.05 \text{ inches Hg}$$

DRY MOLE FRACTION OF FLUE GAS

$$\text{Mfd} = 1 - \%H_2O / 100$$

$$\text{Mfd} = 1 - 18.5/100 = 0.815$$

DRY MOLECULAR WEIGHT OF FLUE GAS

$$\text{Md} = (\%CO_2/100 * 44) + (\%O_2/100 * 32) + ((100 - \%CO_2 - \%O_2)/100 * 28)$$

$$\text{Md} = (10.0/100 * 44) + (10.8/100 * 32) + ((100 - 10.0 - 10.8)/100 * 28)$$

$$\text{Md} = 30.03 \text{ lb/lb-Mole}$$

WET MOLECULAR WEIGHT OF FLUE GAS

$$\text{Ms} = (\text{Md} * \text{Mfd}) + (0.18 * \%H_2O)$$

$$\text{Ms} = (30.03 * 0.815) + (0.18 * 18.5) = 27.80 \text{ lb/lb-Mole}$$

AVERAGE FLUE GAS VELOCITY [Note: (Delta p)avg is square of average square root]

$$vs = 85.49 * Cp * \text{SQUARE ROOT}\left[\frac{(\text{Delta P})avg * (460 + ts)}{Ps * Ms}\right]$$

$$vs = 85.49 * 0.840 * \text{SQUARE ROOT}\left[\frac{0.4774 * (460 + 268)}{29.05 * 27.80}\right] = 47.11 \text{ ft/sec}$$

DRY VOLUMETRIC FLUE GAS FLOW RATE AT STANDARD CONDITIONS

$$Qsd = \frac{60}{144} * Mfd * vs * A * \frac{Tstd}{460 + ts} * \frac{Ps}{Pstd}$$

$$Qsd = \frac{60}{144} * 0.815 * 47.11 * 9{,}216.0 * \frac{528}{460 + 268} * \frac{29.05}{29.92}$$

Qsd = 103,822 DSCFM

DRY VOLUMETRIC FLUE GAS FLOW RATE AT STANDARD CONDITIONS

Qmsd = Qsd * 0.02832

Qmsd = 103,822 * 0.02832 = 2,940 DSCMM

WET VOLUMETRIC FLUE GAS FLOW RATE AT ACTUAL CONDITIONS

Qaw = 60 / 144 * vs * A

Qaw = 60 / 144 * 47.11 * 9,216.0 = 180,902 ACFM

PERCENT ISOKINETIC OF SAMPLING RATE

$$\%I = \frac{Pstd}{Tstd} * \frac{100}{60} * \frac{(ts + 460) * Vmstd}{Ps * vs * Mfd * Theta * (\pi * (NozzleDia/2)^2/144)}$$

$$\%I = \frac{29.92}{528} * \frac{100}{60} * \frac{(268 + 460) * 111.228}{29.05 * 47.11 * 0.815 * 125.00 * (\pi * (0.316/2)^2/144)}$$

%I = 100.7 %

PERCENT EXCESS AIR

$$\%EA = \frac{\%O_2 - (0.5 * \%CO)}{0.264 * (100 - \%CO_2 - \%O_2) - (\%O_2 - (0.5 * \%CO))} * 100$$

$$\%EA = \frac{10.8 - (0.5 * 0.0)}{0.264 * (100 - 10.0 - 10.8) - (10.8 - (0.5 * 0.0))} * 100 = 107.0 \%$$

APPROXIMATE HEAT INPUT RATE

$$10^6\text{Btu/hr} = 60 * \frac{\text{Qsd}}{\text{F}} * \frac{20.9 - \%O_2}{20.9}$$

$$10^6\text{Btu/hr} = 60 * \frac{103{,}822}{9{,}685} * \frac{20.9 - 10.8}{20.9} = \quad 311.0 \quad \text{Million Btu/hr}$$

CONCENTRATION, MILLIGRAMS PER DRY STANDARD CUBIC METER, FILTERABLE PARTICULATE

$$\text{mg/DSCM} = \frac{(\text{mg} \,/\, 10^3)}{\text{Vmstd} * 0.02832} * 10^3$$

$$\text{mg/DSCM} = \frac{(25.3/10^3)}{111.228 * 0.02832} * 10^3 = \quad 8.03 \quad \text{mg/DSCM}$$

CONCENTRATION, MILLIGRAMS PER DSCM CORRECTED TO 12% CO_2, FILTERABLE PARTICULATE

$$\text{mgDSCM@12\%} = \text{mg/DSCM} * (12 \,/\, \%CO_2)$$

$$\text{mgDSCM@12\%} = \quad 8.03 * (12 \,/\, 10.0) = \quad 9.64 \quad \text{mg/DSCM @ 12\% } CO_2$$

CONCENTRATION, MILLIGRAMS PER DSCM CORRECTED TO 7% O_2, FILTERABLE PARTICULATE

$$\text{mgDSCM@7\%} = \text{mg/DSCM} * \frac{21.0 - 7}{21.0 - \%O_2}$$

$$\text{mgDSCM@7\%} = \quad 8.03 * \frac{21.0 - 7}{21.0 - 10.8} = \quad 11.0 \quad \text{mg/DSCM @ 7\% } O_2$$

CONCENTRATION, GRAINS PER DRY STANDARD CUBIC FOOT, FILTERABLE PARTICULATE

$$\text{gr/DSCF} = \frac{7{,}000}{453.592} * \frac{(\text{mg} \,/\, 10^3)}{\text{Vmstd}}$$

$$\text{gr/DSCF} = \frac{7{,}000}{453.592} * \frac{(25.3/10^3)}{111.228} = \quad 0.00351 \quad \text{gr/DSCF}$$

CONCENTRATION, GRAINS PER DSCF CORRECTED TO 12% CO_2, FILTERABLE PARTICULATE

$$\text{gr@12\%} = \text{gr/DSCF} * (12 \,/\, \%CO_2)$$

$$\text{gr@12\%} = \quad 0.00351 * (12 \,/\, 10.0) = \quad 0.00421 \quad \text{gr/DSCF @ 12\% } CO_2$$

CONCENTRATION, GRAINS PER DSCF CORRECTED TO 7% O_2, FILTERABLE PARTICULATE

$$gr@7\% = gr/DSCF * \frac{21.0 - 7}{21.0 - \%O_2}$$

$$gr@7\% = 0.00351 * \frac{21.0 - 7}{21.0 - 10.8} = 0.00482 \quad gr/DSCF\ @\ 7\%\ O_2$$

EMISSION RATE, POUNDS PER HOUR, FILTERABLE PARTICULATE

$$lb/hr = \frac{60}{453.592} * \frac{(mg / 10^3)}{Vmstd} * Qsd$$

$$lb/hr = \frac{60}{453.592} * \frac{(25.3/10^3)}{111.228} * 103{,}822 = 3.12 \quad lb/hr$$

EMISSION RATE, POUNDS PER MILLION BTU, FILTERABLE PARTICULATE

$$lb/10^6Btu = \frac{lbs}{DSCF} \times \frac{Fd\ DSCF\ at\ 12\%\ CO_2}{MMBtu}$$

CONCENTRATION, MICROGRAMS PER DRY STANDARD CUBIC METER, ANTIMONY

$$ug/DSCM = \frac{(ug / 10^6)}{Vmstd * 0.02832} * 10^6$$

$$ug/DSCM = \frac{(86.0/10^6)}{111.228 * 0.02832} * 10^6 = 27.3 \quad ug/DSCM$$

CONCENTRATION, MICROGRAMS PER DSCM CORRECTED TO 12% CO_2, ANTIMONY

$$ugDSCM@12\% = ug/DSCM * (12 / \%CO_2)$$

$$ugDSCM@12\% = 27.3 * (12 / 10.0) = 32.8 \quad ug/DSCM\ @\ 12\%\ CO_2$$

CONCENTRATION, MICROGRAMS PER DSCM CORRECTED TO 7% O_2, ANTIMONY

$$\text{ugDSCM@7\%} = \text{ug/DSCM} * \frac{21.0 - 7}{21.0 - \%O_2}$$

$$\text{ugDSCM@7\%} = 27.3 * \frac{21.0 - 7}{21.0 - 10.8} = 37.5 \ \text{ug/DSCM @ 7\% } O_2$$