

Title 40 -- Protection of Environment; Revised as of July 1, 1991

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

§ 60. Appendix A to Part 60 -- Test Methods [PART I OF VII]

**40 CFR 60. Appendix A** to Part 60

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The test methods in this appendix are referred to in § 60.8 (Performance Tests) and § 60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title "Test Methods and Procedures" is provided to: (1) Identify

the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. Section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as "subject to the approval of the Administrator" or as "or equivalent." Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

## 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 m<sup>2</sup> (113 in.<sup>2</sup>) 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:

$$D[e] = 2LW / (L + W)$$

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 procedure, 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.

DUCT DIAMETERS UPSTREAM FROM FLOW DISTURBANCE \* (DISTANCE A)

DUCT DIAMETERS DOWNSTREAM FROM FLOW DISTURBANCE \* (DISTANCE B)

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

[SEE FIGURE IN ORIGINAL]

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	3 x 3
12	4 x 3
16	4 x 4
20	5 x 4
25	5 x 5
30	6 x 5
36	6 x 6
42	7 x 6
49	7 x 7

DUCT DIAMETERS UPSTREAM FROM FLOW DISTURBANCE (DISTANCE A)

DUCT DIAMETERS DOWNSTREAM FROM FLOW DISTURBANCE (DISTANCE B)

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

[SEE FIGURE IN ORIGINAL]

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 101.

### 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.

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

[SEE FIGURE IN ORIGINAL]

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
1	14.6	6.7	4.4	3.2	2.6	2.1
2	85.4	25.0	14.6	10.5	8.2	6.7
3		75.0	29.6	19.4	14.6	11.8
4		93.3	70.4	32.3	22.6	17.7
5			85.4	67.7	34.2	25.0
6			95.6	80.6	65.8	35.6
7				89.5	77.4	64.4
8				96.8	85.4	75.0
9					91.8	82.3
10					97.4	88.2
11						93.3
12						97.9
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						

Traverse point number on a diameter	Number of traverse points on a diameter--					
	14	16	18	20	22	24
1	1.8	1.6	1.4	1.3	1.1	1.1

2	5.7	4.9	4.4	3.9	3.5	3.2
3	9.9	8.5	7.5	6.7	6.0	5.5
4	14.6	12.5	10.9	9.7	8.7	7.9
5	20.1	16.9	14.6	12.9	11.6	10.5
6	26.9	22.0	18.8	16.5	14.6	13.2
7	36.6	28.3	23.6	20.4	18.0	16.1
8	63.4	37.5	29.6	25.0	21.8	19.4
9	73.1	62.5	38.2	30.6	26.2	23.0
10	79.9	71.7	61.8	38.8	31.5	27.2
11	85.4	78.0	70.4	61.2	39.3	32.3
12	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 4 x 3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9 x 4 or 12 x 3, and would not necessarily have to be 6 x 6. 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.

[SEE FIGURE IN ORIGINAL]

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 deg. reference." Note the differential pressure (DELTA<sub>p</sub>) reading at each traverse point. If a null (zero) pitot reading is obtained at 0 deg. reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0 deg. reference, rotate the pitot tube (up to + / -90 deg. yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (alpha) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of alpha: assign alpha values of 0 degrees to those points for which no rotation was required, and include these in the overall average. If the average value of alpha is greater than 20 degrees, 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.

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 1/2 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 "backpurging" 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, section 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, section 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 section 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<sub>2</sub>O 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 section 2.5.3.1 is required. If the criteria for a leakfree 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:

$$R[1]=\text{arc cosine}[(\text{cosine } Y[1])(\text{cosine } P[1])]$$

Eq. 1-2

Where:

R[1]=Resultant angle at traverse point i, degree.

Y[1]=Yaw angle at traverse point i, degree.

P[1]=Pitch angle at traverse point i, degree.

2.5.4.2 Calculate the average resultant for the measurements:

$$R = \text{SIGMA } R[1] / n$$

Eq. 1-3

Where:

R =Average resultant angle, degree.

n=Total number of traverse points.

2.5.4.3 Calculate the standard deviations:

$$S[d] = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (R[i] - R)^2}$$

Eq. 1-4

Where:

S[d] = Standard deviation, deg.

2.5.5 The measurement location is acceptable if  $R \leq 20$  deg. and  $S[d] \leq 10$  deg.

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 ft/min).

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 deg. apart. The gas flow angle measured in each port must be  $\pm 2$  deg. of 0 deg. 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 deg. increments for angles from -60 deg. to +60 deg. 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 deg. for angles between 0 deg. and 40 deg. and within 3 deg. for angles between 40 deg. and 60 deg.

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-dimensional probe. This should be within 2 deg. of 0 deg. 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.

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## METHOD 1A -- SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES WITH SMALL STACKS OR DUCTS

### *1. Applicability and Principle*

1.1 The applicability and principle of this method are identical to Method 1, except this method's applicability is

limited to stacks or ducts less than about 0.30 meter (12 in.) in diameter or 0.071 m<sup>2</sup> (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter or 0.0081 m<sup>2</sup> (12.57 in.<sup>2</sup>) in cross-sectional area.

1.2 In these small diameter stacks or ducts, the conventional Method 5 stack assembly (consisting of a Type S pitot tube attached to a sampling probe, equipped with a nozzle and thermocouple) blocks a significant portion of the cross section of the duct and causes inaccurate measurements. Therefore, for particulate matter (PM) sampling in small stacks or ducts, the gas velocity is measured using a standard pitot tube downstream of the actual emission sampling site. The straight run of duct between the PM sampling and velocity measurement sites allows the flow profile, temporarily disturbed by the presence of the sampling probe, to redevelop and stabilize.

1.3 The cross-sectional layout and location of traverse points and the verification of the absence of cyclonic flow are the same as in Method 1, Sections 2.3 and 2.4, respectively. Differences from Method 1, except as noted, are given below.

## 2. Procedure

### 2.1 Selection of Sampling and Measurement Sites.

2.1.1 PM Measurements. Select a PM sampling site located preferably at least 8 equivalent stack or duct diameters downstream and 10 equivalent diameters upstream from any flow disturbances such as bends, expansions, or contractions in the stack, or from a visible flame. Next, locate the velocity measurement site 8 equivalent diameters downstream of the PM sampling site. See Figure 1A-1. If such locations are not available, select an alternative PM sampling site that is at least 2 equivalent stack or duct diameters downstream and 2 1/2 diameters upstream from any flow disturbance. Then, locate the velocity measurement site 2 equivalent diameters downstream from the PM sampling site. Follow Section 2.1 of Method 1 for calculating equivalent diameters for a rectangular cross section.

Figure 1A-1. Recommended sampling arrangement for small ducts.

[SEE FIGURE IN ORIGINAL]

2.1.2 PM Sampling (Steady Flow) or only Velocity Measurements. For PM sampling when the volumetric flow rate in a duct is constant with respect to time, Section 2.1 of Method 1 may be followed, with the PM sampling and velocity measurement performed at one location. To demonstrate that the flow rate is constant (within 10 percent) when PM measurements are made, perform complete velocity traverses before and after the PM sampling run, and calculate the deviation of the flow rate derived after the PM sampling run from the one derived before the PM sampling run. The PM sampling run is acceptable if the deviation does not exceed 10 percent.

### 2.2 Determining the Number of Traverse Points.

2.2.1 PM Sampling. Use Figure 1-1 of Method 1 to determine the number of traverse points to use at both the velocity measurement and PM sampling locations. Before referring to the figure, however, determine the distances between both the velocity measurement and PM sampling sites to the nearest upstream and downstream disturbances. Then divide each distance by the stack diameter or equivalent diameter to express the distances in terms of the number of duct diameters. Next, determine the number of traverse points from Figure 1-1 of Method 1 corresponding to each of these four distances. Choose the highest of the four numbers of traverse points (or a greater number) so that, for circular ducts, the number is a multiple of four, and for rectangular ducts, the number is one of those shown in Table 1-1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular

ducts and nine for rectangular ducts.

2.2.2 PM Sampling (Steady Flow) or Velocity Measurements. Use Figure 1-2 of Method 1 to determine the number of traverse points, following the same procedure used for PM sampling traverses as described in Section 2.2.1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular ducts and nine for rectangular ducts.

### 3. Bibliography

1. Same as in Method 1, Section 3, Citations 1 through 6.

2. Vollaro, Robert F. Recommended Procedure for Sample Traverses in Ducts Smaller Than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. January 1977.

## 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.

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

[SEE FIGURE IN ORIGINAL]

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 centimeter (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.

[SEE FIGURE IN ORIGINAL]

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.

[SEE FIGURE IN ORIGINAL]

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  $C_p(s)$  so long as  $\alpha[1]$  and  $\alpha[2] \leq 10$  deg.,  $\beta[1]$  and  $\beta[2] \leq 5$  deg.,  $z \leq 0.32$  cm (1/8 in.) and  $2 \leq 0.08$  cm (1/32 in.) (citation 11 in Bibliography).

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 (DELTA p) 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 DELTA p reading. If the DELTA p readings made before and after the air purge are the same (+/- 5 percent), the traverse is acceptable. Otherwise, reject the run. Note that if DELTA p 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 DELTA p readings shall be taken, as above, for the last two back purges at which suitably high DELTA p 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<sub>2</sub>O divisions on the 0-to 1-in. inclined scale, and 0.1-in. H<sub>2</sub>O 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 DELTA p values as low as 1.3 mm (0.05 in.) H<sub>2</sub>O. 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 DELTA p readings at the traverse points in the stack is less than 1.3 mm (0.05 in.) H<sub>2</sub>O; (2) for traverses of 12 or more points, more than 10 percent of the individual DELTA p readings are below 1.3 mm (0.05 in.) H<sub>2</sub>O; (3) for traverses of fewer than 12 points, more than one DELTA p reading is below 1.3 mm (0.05 in.) H<sub>2</sub>O. Citation 18 in Bibliography 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:

$$T = \langle n \rangle \text{SIGMA } [i = 1] \text{ root DELTA } p[i] + K / \langle n \rangle \text{SIGMA } [i = 1] \text{ root DELTA } p[i]$$

Where:

DELTA p[i] = Individual velocity head reading at a traverse point, mm H<sub>2</sub>O (in. H<sub>2</sub>O).

n = Total number of traverse points.

K = 0.13 mm H<sub>2</sub>O when metric units are used and 0.005 in. H<sub>2</sub>O 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 DELTA  $p$  readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of DELTA  $p$  values in the stack. If, at each point, the values of DELTA  $p$  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 DELTA  $p$  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). Alternative 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 Bibliography) 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 deg. bend.

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

2.7.5 Ninety deg. 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<sub>2</sub>O (0.005 in. H<sub>2</sub>O). For multivelocity calibrations, the gauge shall be readable to the nearest 0.13 mm H<sub>2</sub>O (0.005 in. H<sub>2</sub>O) for DELTA p values between 1.3 and 25 mm H<sub>2</sub>O (0.05 and 1.0 in. H<sub>2</sub>O), and to the nearest 1.3 mm H<sub>2</sub>O (0.05 in. H<sub>2</sub>O) for DELTA p values above 25 mm H<sub>2</sub>O (1.0 in. H<sub>2</sub>O). A special, more sensitive gauge will be required to read DELTA p values below 1.3 mm H<sub>2</sub>O [0.05 in. H<sub>2</sub>O] (see Citation 18 in Bibliography).

Figure 2-4. Standard pitot tube design specifications.

[SEE FIGURE IN ORIGINAL]

### 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 DELTA p 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<sub>2</sub>O 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<sub>2</sub>O. 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 DELTA p values encountered (see Section 2.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the DELTA p 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.

Figure 2-5. Velocity traverse data.

[SEE FIGURE IN ORIGINAL]

3.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO<sub>2</sub>, O<sub>2</sub>, CO, and N<sub>2</sub>, 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 specified limits, the pitot tube must be calibrated as outlined in 4.1.2 through 4.1.5 below.

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 Bibliography); 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 2-6. 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.).

[SEE FIGURE IN ORIGINAL]

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.).

[SEE FIGURE IN ORIGINAL]

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:

$$D[e] = 2LW / (L + W)$$

Eq. 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 Bibliography 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.

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 care 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 DELTA p[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 DELTA p[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 DELTA p 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 DELTA p 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 tube coefficient as follows:

Figure 2-9. Pitot tube calibration data.

[SEE FIGURE IN ORIGINAL]

$$C[p(s)] = C[p(std)] \times \sqrt{\text{DELTA } p[\text{std}] / \text{DELTA } p[s]}$$

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.

DELTA p[std] = Velocity head measured by the standard pitot tube, cm H<sub>2</sub>O (in. H<sub>2</sub>O)

DELTA p[s] = Velocity head measured by the Type S pitot tube, cm H<sub>2</sub>O (in. H<sub>2</sub>O)

4.1.4.2 Calculate  $C[p]$  (side A), the mean A-side coefficient, and  $C[p]$  (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  $C[p(s)]$  from  $C[p]$  (side A), and the deviation of each B-side value of  $C[p(s)]$  from  $C[p]$  (side B). Use the following equation:

$$\text{Deviation} = C[p(s)] - C[p] \text{ (A or B)}$$

Equation 2-3

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

$$\text{sigma (side A or B)} = \frac{\sum [C[p(s)] - C[p] \text{ (A or B)}]}{3}$$

Equation 2-4

4.1.4.5 Use the Type S pitot tube only if the values of sigma (side A) and sigma (side B) are less than or equal to 0.01 and if the absolute value of the difference between  $C[p]$  (A) and  $C[p]$  (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.,  $C[p]$  (side A) and  $C[p]$  (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 Bibliography). 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 1/4 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 (sigma) value of

0.01 or less (see Section 4.1.4.4).

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

[SEE FIGURE IN ORIGINAL]

#### 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 Bibliography for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches (Citation 16 in Bibliography).

##### 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 damaged 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 degrees C (761 degrees 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 degrees C (761 degrees 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, m<sup>2</sup> (ft<sup>2</sup>).

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 m/sec [(g/g-mole) (mm Hg) / (deg. K) (mm H<sub>2</sub>O)]<sup>1/2</sup>

for the metric system and

85.49 ft/sec [(lb/lb-mole) (in. Hg) / (deg. R) (in. H<sub>2</sub>O)]<sup>1/2</sup>

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] X (1 - B[ws]) + 18.0 B[ws]

Eq. 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]

Eq. 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, deg. C (deg. F).

T[s] = Absolute stack temperature, deg. K, (deg. R). = 273 + t[s] for metric.

Eq. 2-7

= 460 + t[s] for English.

Eq. 2-8

T[std] = Standard absolute temperature, 293 deg. K (528 deg. R).

v[s] = Average stack gas velocity, m/sec (ft/sec).

DELTA p = Velocity head of stack gas, mm H<sub>2</sub>O (in. H<sub>2</sub>O).

3,600 = Conversion factor, sec/hr.

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

5.2 Average Stack Gas Velocity.

$v[s] = K[p] \times C[p] \times (\text{root DELTA } p)[\text{avg}] \times \text{root } T[s(\text{avg})] / (P[s] \times M[s])$

Equation 2-9

5.3 Average Stack Gas Dry Volumetric Flow Rate.

$Q[\text{sd}] = 3,600 \times (1 - B[\text{ws}]) \times v[s] \times A \times (T[\text{std}] / T[s(\text{avg})]) \times (P[s] / P[\text{std}])$

Eq. 2-10

To convert Q[sd] from dscm/hr (dscf/hr) to dscm/min (dscf/min), divide Q[sd] by 60.

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## METHOD 2A -- DIRECT MEASUREMENT OF GAS VOLUME THROUGH PIPES AND SMALL DUCTS

### 1. *Applicability and Principle*

1.1 Applicability. This method applies to the measurement of gas flow rates in pipes and small ducts, either in-line or at exhaust positions, within the temperature range of 0 to 50 degrees C.

1.2 Principle. A gas volume meter is used to measure gas volume directly. Temperature and pressure measurements are made to correct the volume to standard conditions.

### 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 Gas Volume Meter. A positive displacement meter, turbine meter, or other direct volume measuring device capable of measuring volume to within 2 percent. The meter shall be equipped with a temperature gauge (+/- 2 percent of the minimum absolute temperature) and a pressure gauge (+/- 2.5 mm Hg). The manufacturer's recommended capacity of the meter shall be sufficient for the expected maximum and minimum flow rates at the sampling conditions. Temperature, pressure, corrosive characteristics, and pipe size are factors necessary to consider in choosing a suitable gas meter.

2.2 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm 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 the sampling point shall be applied at a rate of minus 2.5 mm Hg per 30-meter elevation increase, or vice-versa for elevation decrease.

2.3 Stopwatch. Capable of measurement to within 1 second.

### 3. Procedure

3.1 Installation. As there are numerous types of pipes and small ducts that may be subject to volume measurement, it would be difficult to describe all possible installation schemes. In general, flange fittings should be used for all connections wherever possible. Gaskets or other seal materials should be used to assure leak-tight connections. The volume meter should be located so as to avoid severe vibrations and other factors that may affect the meter calibration.

3.2 Leak Test. A volume meter installed at a location under positive pressure may be leak-checked at the meter connections by using a liquid leak detector solution containing a surfactant. Apply a small amount of the solution to the connections. If a leak exists, bubbles will form, and the leak must be corrected.

A volume meter installed at a location under negative pressure is very difficult to test for leaks without blocking flow at the inlet of the line and watching for meter movement. If this procedure is not possible, visually check all connections and assure tight seals.

### 3.3 Volume Measurement.

3.3.1 For sources with continuous, steady emission flow rates, record the initial meter volume reading, meter temperature(s), meter pressure, and start the stopwatch. Throughout the test period, record the meter temperature(s) and pressure so that average values can be determined. At the end of the test, stop the timer and record the elapsed time, the final volume reading, meter temperature(s), and pressure. Record the barometric pressure at the beginning and end of the test run. Record the data on a table similar to Figure 2A-1.

Figure 2A-1. Volume flow rate measurement data.

[SEE FIGURE IN ORIGINAL]

3.3.2 For sources with noncontinuous, non-steady emission flow rates, use the procedure in 3.3.1 with the addition of the following: Record all the meter parameters and the start and stop times corresponding to each process cyclical or noncontinuous event.

### 4. Calibration

4.1 Volume Meter. The volume meter is calibrated against a standard reference meter prior to its initial use in the field. The reference meter is a spirometer or liquid displacement meter with a capacity consistent with that

of the test meter.

Alternatively, a calibrated, standard pitot may be used as the reference meter in conjunction with a wind tunnel assembly. Attach the test meter to the wind tunnel so that the total flow passes through the test meter. For each calibration run, conduct a 4-point traverse along one stack diameter at a position at least eight diameters of straight tunnel downstream and two diameters upstream of any bend, inlet, or air mover. Determine the traverse point locations as specified in Method 1. Calculate the reference volume using the velocity values following the procedure in Method 2, the wind tunnel cross-sectional area, and the run time.

Set up the test meter in a configuration similar to that used in the field installation (i.e., in relation to the flow moving device). Connect the temperature and pressure gauges as they are to be used in the field. Connect the reference meter at the inlet of the flow line, if appropriate for the meter, and begin gas flow through the system to condition the meters. During this conditioning operation, check the system for leaks.

The calibration shall be run over at least three different flow rates. The calibration flow rates shall be about 0.3, 0.6, and 0.9 times the test meter's rated maximum flow rate.

For each calibration run, the data to be collected include: reference meter initial and final volume readings, the test meter initial and final volume reading, meter average temperature and pressure, barometric pressure, and run time. Repeat the runs at each flow rate at least three times.

Calculate the test meter calibration coefficient,  $Y[m]$ , for each run as follows:

$$Y[m] = (V[rf] - V[ri]) (t[r] + 273) / (V[mf] - V[mi]) (t[m] + 273) P[b] / (P[b] + P[g])$$

Eq. 2A-1

Where:

$Y[m]$  = Test volume meter calibration coefficient, dimensionless.

$V[r]$  = Reference meter volume reading, m<sup>3</sup>.

$V[m]$  = Test meter volume reading, m<sup>3</sup>.

$t[r]$  = Reference meter average temperature, degrees C.

$t[m]$  = Test meter average temperature, degrees C.

$P[b]$  = Barometric pressure, mm Hg.

$P[g]$  = Test meter average static pressure, mm Hg.

f = Final reading for run.

i = Initial reading for run.

Compare the three  $Y[m]$  values at each of the flow rates tested 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 runs may be required to complete this requirement. If this specification cannot be met in six successive runs, the test meter is not suitable for use. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications are met at all the flow rates, average all the  $Y[m]$  values from runs meeting the

specifications to obtain an average meter calibration coefficient,  $Y[m]$ .

The procedure above shall be performed at least once for each volume meter. Thereafter, an abbreviated calibration check shall be completed following each field test. The calibration of the volume meter shall be checked by performing three calibration runs at a single, intermediate flow rate (based on the previous field test) with the meter pressure set at the average value encountered in the field test. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of flow as described above.

NOTE. -- If the volume meter calibration 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 greater value of pollutant emission rate.

4.2 Temperature Gauge. After each test series, check the temperature gauge at ambient temperature. Use an American Society for Testing and Materials (ASTM) mercury-in-glass reference thermometer, or equivalent, as a reference. If the gauge being checked agrees within 2 percent (absolute temperature) of the reference, the temperature data collected in the field shall be considered valid. Otherwise, the test data shall be considered invalid or adjustments of the test results shall be made, subject to the approval of the Administrator.

4.3 Barometer. Calibrate the barometer used against a mercury barometer prior to the field test.

## 5. Calculations

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

### 5.1 Nomenclature.

$P[b]$  = Barometric pressure, mm Hg.

$P[g]$  = Average static pressure in volume meter, mm Hg.

$Q[s]$  = Gas flow rate,  $m^3/min$ , standard conditions.

$T[m]$  = Average absolute meter temperature, degrees K.

$V[m]$  = Meter volume reading,  $m^3$ .

$Y[m]$  = Average meter calibration coefficient, dimensionless.

$f$  = Final reading for test period.

$i$  = Initial reading for test period.

$s$  = Standard conditions, 20 degrees C and 760 mm Hg.

THETA = Elapsed test period time, min.

### 5.2 Volume.

$V[ms] = 0.3853 Y[m] (V[mf] - V[mi]) (P[b] + P[g] / T[m])$

Eq. 2A-2

5.3 Gas Flow Rate.

$$Q[s] = V[ms] / \text{THETA}$$

Eq. 2A-3

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## METHOD 2B -- DETERMINATION OF EXHAUST GAS VOLUME FLOW RATE FROM GASOLINE VAPOR INCINERATORS

### 1. *Applicability and Principle*

1.1 Applicability. This method applies to the measurement of exhaust volume flow rate from incinerators that process gasoline vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). It is assumed that the amount of auxiliary fuel is negligible.

1.2 Principle. The incinerator exhaust flow rate is determined by carbon balance. Organic carbon concentration and volume flow rate are measured at the incinerator inlet. Organic carbon, carbon dioxide (CO<sub>2</sub>), and carbon monoxide (CO) concentrations are measured at the outlet. Then the ratio of total carbon at the incinerator inlet and outlet is multiplied by the inlet volume to determine the exhaust volume and volume flow rate.

### 2. *Apparatus*

- 2.1 Volume Meter. Equipment described in Method 2A.
- 2.2 Organic Analyzers (2). Equipment described in Method 25A or 25B.
- 2.3 CO Analyzer. Equipment described in Method 10.
- 2.4 CO<sub>2</sub> Analyzer. A nondispersive infrared (NDIR) CO<sub>2</sub> analyzer and supporting equipment with comparable specifications as CO analyzer described in Method 10.

### 3. *Procedure*

3.1 Inlet Installation. Install a volume meter in the vapor line to incinerator inlet according to the procedure in Method 2A. At the volume meter inlet, install a sample probe as described in Method 25A. Connect to the probe a leak-tight, heated (if necessary to prevent condensation) sample line (stainless steel or equivalent) and an organic analyzer system as described in Method 25A or 25B.

3.2 Exhaust Installation. Three sample analyzers are required for the incinerator exhaust: CO<sub>2</sub>, CO, and

organic analyzers. A sample manifold with a single sample probe may be used. Install a sample probe as described in Method 25A. Connect a leak-tight heated sample line to the sample probe. Heat the sample line sufficiently to prevent any condensation.

3.3 Recording Requirements. The output of each analyzer must be permanently recorded on an analog strip chart, digital recorder, or other recording device. The chart speed or number of readings per time unit must be similar for all analyzers so that data can be correlated. The minimum data recording requirement for each analyzer is one measurement value per minute.

3.4 Preparation. Prepare and calibrate all equipment and analyzers according to the procedures in the respective methods. For the CO<sub>2</sub> analyzer, follow the procedures described in Method 10 for CO analysis substituting CO<sub>2</sub> calibration gas where the method calls for CO calibration gas. The span value for the CO<sub>2</sub> analyzer shall be 15 percent by volume. All calibration gases must be introduced at the connection between the probe and the sample line. If a manifold system is used for the exhaust analyzers, all the analyzers and sample pumps must be operating when the calibrations are done. Note: For the purposes of this test, methane should not be used as an organic calibration gas.

3.5 Sampling. At the beginning of the test period, record the initial parameters for the inlet volume meter according to the procedures in Method 2A and mark all of the recorder strip charts to indicate the start of the test. Continue recording inlet organic and exhaust CO<sub>2</sub>, CO, and organic concentrations throughout the test. During periods of process interruption and halting of gas flow, stop the timer and mark the recorder strip charts so that data from this interruption are not included in the calculations. At the end of the test period, record the final parameters for the inlet volume meter and mark the end on all of the recorder strip charts.

3.6 Post Test Calibrations. At the conclusion of the sampling period, introduce the calibration gases as specified in the respective reference methods. If an analyzer output does not meet the specifications of the method, invalidate the test data for the period. Alternatively, calculate the volume results using initial calibration data and using final calibration data and report both resulting volumes. Then, for emissions calculations, use the volume measurement resulting in the greatest emission rate or concentration.

#### 4. Calculations

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

##### 4.1 Nomenclature.

CO[e] = Mean carbon monoxide concentration in system exhaust, ppm.

CO<sub>2</sub>[e] = Mean carbon dioxide concentration in system exhaust, ppm.

HC[e] = Mean organic concentration in system exhaust as defined by the calibration gas, ppm.

HC[i] = Mean organic concentration in system inlet as defined by the calibration gas, ppm.

K = Calibration gas factor

= 2 for ethane calibration gas.

= 3 for propane calibration gas.

= 4 for butane calibration gas.

= Appropriate response factor for other calibration gas.

$V_{[es]}$  = Exhaust gas volume, m<sup>3</sup>.

$V_{[is]}$  = Inlet gas volume, m<sup>3</sup>.

$Q_{[es]}$  = Exhaust gas volume flow rate, m<sup>3</sup>/min.

$Q_{[is]}$  = Inlet gas volume flow rate, m<sup>3</sup>/min.

<SO> = Sample run time, min.

s = Standard conditions: 20 degrees C, 760 mm Hg.

300 = Estimated concentration of ambient CO<sub>2</sub>, ppm. (CO<sub>2</sub> concentration in the ambient air may be measured during the test period using an NDIR).

4.2 Concentrations. Determine mean concentrations of inlet organics, outlet CO<sub>2</sub>, outlet CO, and outlet organics according to the procedures in the respective methods and the analyzers' calibration curves, and for the time intervals specified in the applicable regulations. Concentrations should be determined on a parts per million by volume (ppm) basis.

4.3 Exhaust Gas Volume. Calculate the exhaust gas volume as follows:

$$V_{[es]} = V_{[is]} \left[ \frac{K(HC[i])}{K(HC[e]) + CO_{2e} + CO[e]} - 300 \right]$$

Eq. 2B-1

4.4 Exhaust Gas Volume Flow Rate. Calculate the exhaust gas volume flow rate as follows:

$$Q_{[es]} = V_{[es]} / \theta$$

Eq. 2B-2

## 5. Bibliography

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### METHOD 2C -- DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE IN SMALL STACKS OR DUCTS (STANDARD PITOT TUBE)

#### 1. Applicability and Principle

##### 1.1 Applicability.

1.1.1 The applicability of this method is identical to Method 2, except this method is limited to stationary source stacks or ducts less than about 0.30 meter (12 in.) in diameter or 0.071 m<sup>2</sup> (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter or 0.0081 m<sup>2</sup> (12.57 in.<sup>2</sup>) in cross-sectional area.

1.1.2 The apparatus, procedure, calibration, calculations, and bibliography are the same as in Method 2, Sections 2, 3, 4, 5, and 6, except as noted in the following sections.

1.2 Principle. The average gas velocity in a stack or duct is determined from the gas density and from measurement of velocity heads with a standard pitot tube.

## 2. Apparatus

2.1 Standard Pitot Tube (instead of Type S). Use a standard pitot tube that meets the specifications of Section 2.7 of Method 2. Use a coefficient value of 0.99 unless it is calibrated against another standard pitot tube with an NBS-traceable coefficient.

2.2 Alternative Pitot Tube. A modified hemispherical-nosed pitot tube (see Figure 2C-1), which features a shortened stem and enlarged impact and static pressure holes, may be used. This pitot tube is useful in liquid drop-laden gas streams when a pitot "back purge" is ineffective. Use a coefficient value of 0.99 unless the pitot is calibrated as mentioned in Section 2.1 above.

Figure 2C-1. Modified hemispherical-nosed pitot tube.

[SEE FIGURE IN ORIGINAL]

## 3. Procedure

Follow the general procedures in Section 3 of Method 2, except conduct the measurements at the traverse points specified in Method 1A. The static and impact pressure holes of standard pitot tubes are susceptible to plugging in PM-laden gas streams. Therefore, the tester must furnish adequate proof that the openings of the pitot tube have not plugged during the traverse period; this proof can be obtained by first recording the velocity head (DELTA p) reading at the final traverse point, then cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and finally by recording another DELTA p reading at the final traverse point. If the DELTA p reading made after the air purge is within 5 percent of the reading during the traverse, then the traverse is acceptable. Otherwise, reject the run. Note that if the DELTA p at the final traverse point is so low as to make this determination too difficult, then another traverse point may be selected. If "back purging" at regular intervals is part of the procedure, then take comparative DELTA p readings, as above, for the last two back purges at which suitable high DELTA p readings are observed.

## METHOD 2D -- MEASUREMENT OF GAS VOLUMETRIC FLOW RATES IN SMALL PIPES AND DUCTS

### 1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of gas flow rates in small pipes and ducts, either before or after emission control devices.

1.2 Principle. To measure flow rate or pressure drop, all the stack gas is directed through a rotameter, orifice plate or similar flow rate measuring device. The measuring device has been previously calibrated in a manner that insures its proper calibration for the gas or gas mixture being measured. Absolute temperature and pressure measurements are also made to calculate volumetric flow rates at standard conditions.

### 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 Flow Rate Measuring Device. A rotameter, orifice plate, or other flow rate measuring device capable of measuring all the stack flow rate to within 5 percent of its true value. The measuring device shall be equipped with a temperature gauge accurate to within 2 percent of the minimum absolute stack temperature and a pressure gauge accurate to within 5 mm Hg. The capacity of the measuring device shall be sufficient for the expected maximum and minimum flow rates at the stack gas conditions. The magnitude and variability of stack gas flow rate, molecular weight, temperature, pressure, compressibility, dew point, corrosiveness, and pipe or duct size are all factors to consider in choosing a suitable measuring device.

2.2 Barometer. Same as in Method 2, Section 2.5.

2.3 Stopwatch. Capable of incremental time measurement to within 1 second.

### 3. Procedure

3.1 Installation. Use the procedure in Method 2A, Section 3.1.

3.2 Leak Check. Use the procedure in Method 2A, Section 3.2.

3.3 Flow Rate Measurement.

3.3.1 Continuous, Steady Flow. At least once an hour, record the measuring device flow rate reading, and the measuring device temperature and pressure. Make a minimum of twelve equally spaced readings of each parameter during the test period. Record the barometric pressure at the beginning and end of the test period. Record the data on a table similar to Figure 2D-1.

Plant

Date Run number

Sample location

Barometric pressure, mm (in.) Hg

Start Finish

Operators

Measuring device number Calibration coefficient

Calibration gas

Last date calibrated

	Static	Temperature
Time	Flow rate reading	pressure
	mm (in.)	
	Hg	degrees C (degrees F)
		degrees K (degrees R)

Average

Figure 2D-1. Flow rate measurement data.

3.3.2 Noncontinuous and Nonsteady Flows. Use flow rate measuring devices with particular caution. Calibration will be affected by variation in stack gas temperature, pressure, compressibility, and molecular weight. Use the procedure in Section 3.3.1. Record all the measuring device parameters on a time interval frequency sufficient to adequately profile each process cyclical or noncontinuous event. A multichannel continuous recorder may be used.

#### 4. Calibration

4.1 Flow Rate Measuring Device. Use the procedure in Method 2A, Section 4, and apply the same performance standards. Calibrate the measuring device with the principal stack gas to be measured (e.g., air, nitrogen) against a standard reference meter. A calibrated dry gas meter is an acceptable reference meter. Ideally, calibrate the measuring device in the field with the actual gas to be measured. For measuring devices that have a volume rate readout, calculate the measuring device calibration coefficient,  $Y[m]$ , for each run as follows:

$$Y[m] = (Q[r]) (T[r]) (P[\text{bar}]) / (Q[m]) (T[m]) (P[\text{bar}] + P[g])$$

Eq. 2D-1

where:

$Q[r]$  = reference meter flow rate reading,  $\text{m}^3/\text{min}$  ( $\text{ft}^3/\text{min}$ ).

$Q[m]$  = measuring device flow rate reading,  $\text{m}^3/\text{min}$  ( $\text{ft}^3/\text{min}$ ).

$T[r]$  = reference meter average absolute temperature, degrees K (degrees R).

$T[m]$  = measuring device average absolute temperature, degrees K (degrees R).

$P[\text{bar}]$  = barometric pressure, mm Hg (in. Hg).

$P[g]$  = measuring device average static pressure, mm Hg (in. Hg).

For measuring devices that do not have a readout as flow rate, refer to the manufacturer's instructions to calculate the  $Q[m]$  corresponding to each  $Q[r]$ .

4.2 Temperature Gauge. Use the procedure and specifications in Method 2A, Section 4.2. Perform the calibration at a temperature that approximates field test conditions.

4.3 Barometer. Calibrate the barometer to be used in the field test with a mercury barometer prior to the field test.

#### 5. Gas Flow Rate Calculation

Calculate the stack gas flow rate,  $Q[s]$ , as follows:

$$Q[s] = K[l] Y[m] Q[m] (P[\text{bar}] + P[\text{g}]) / T[m]$$

Eq. 2D-2

where:

$K[l] = 0.3858$  for international system of units (SI); 17.64 for English units.

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## METHOD 3 -- GAS ANALYSIS FOR THE DETERMINATION OF DRY MOLECULAR WEIGHT

### 1. APPLICABILITY AND PRINCIPLE

#### 1.1 Applicability.

1.1.1 This method is applicable for determining carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) concentrations 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<sub>2</sub>, O<sub>2</sub>, carbon monoxide (CO), and nitrogen (N<sub>2</sub>) are not present in concentrations sufficient to affect the results.

1.1.2 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 multipoint sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO<sub>2</sub> or O<sub>2</sub> and stoichiometric calculations to determine dry molecular weight; and (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 (EPA).

1.1.3 Note. Mention of trade names or specific products does not constitute endorsements by EPA.

1.2 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 CO<sub>2</sub>, percent O<sub>2</sub>, and if necessary, for percent CO. For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used for the analysis.

### 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. Stainless steel or borosilicate glass tubing 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<sub>2</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub> and resistant to temperature at sampling conditions, may be used for the probe. Examples of such materials are aluminum, copper, quartz glass, and Teflon.

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

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. Same as in Section 2.1.1.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser no greater than 250 ml that will not remove O<sub>2</sub>, CO<sub>2</sub>, CO, and N<sub>2</sub>, to remove excess moisture which would interfere with the operation of the pump and flowmeter.

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

Figure 3-2. Integrated gas-sampling train.

[SEE FIGURE IN ORIGINAL]

2.2.4 Pump. A leaf-free, diaphragm-type pump, or equivalent, 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. A rotameter, or equivalent rate meter, capable of measuring flow rate to within 2 percent of the selected flow rate. A flow rate range of 500 to 1000 cc/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. 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<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). 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 (2 to 4 in.) H<sub>2</sub>O 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.), for the flexible bag leak check.

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

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

### 3. SINGLE-POINT, GRAB SAMPLING AND ANALYTICAL PROCEDURE

3.1 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.

3.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight. If

an Orsat analyzer is used, it is recommended that the analyzer be leak checked by following the procedure in Section 6; however, the leak check is optional.

3.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer, and immediately analyze it for percent CO<sub>2</sub> and percent O<sub>2</sub>. Determine the percentage of the gas that is N<sub>2</sub> and CO by subtracting the sum of the percent CO<sub>2</sub> and percent O<sub>2</sub> from 100 percent. Calculate the dry molecular weight as indicated in Section 7.2.

3.4 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 (0.1 lb/lb-mole).

#### 4. SINGLE-POINT, INTEGRATED SAMPLING AND ANALYTICAL PROCEDURE

4.1 The sampling point in the duct shall be located as specified in Section 3.1.

4.2 Leak check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just before 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.

4.3 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<sup>3</sup>) of sample gas is recommended; however, smaller volumes may be collected, if desired.

4.4 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<sub>2</sub> and percent O<sub>2</sub> using either an Orsat analyzer or a Fyrite type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that Orsat leak check described in Section 6, be performed before this determination; however, the check is optional. Determine the percentage of the gas that is N<sub>2</sub> and CO by subtracting the sum of the percent CO<sub>2</sub> and percent O<sub>2</sub> from 100 percent. Calculate the dry molecular weight as indicated in Section 7.2.

4.5 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).

#### 5. MULTI-POINT, INTEGRATED SAMPLING AND ANALYTICAL PROCEDURE

5.1 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 12 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.

5.2 Follow the procedures outlined in Sections 4.2 through 4.5, 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.

Time	Traverse pt.	Q, liter/min	% dev. a
------	-----------------	-----------------	-------------

Average

a % dev. =  $(Q - Q[\text{avg}]) / Q[\text{avg}] \times 100$  (Must be  $\leq \pm 10\%$ )

Figure 3-3. Sampling rate data.

## 6. LEAK-CHECK PROCEDURE FOR ORSAT ANALYZER

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

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

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

6.3 *Record the meniscus position.*

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

6.5 For the Orsat analyzer to pass the leak check, two conditions must be met:

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

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

6.6 If the analyzer fails the leak-check procedure, check all rubber connections and stopcocks to determine whether they might be the cause of the leak. Disassemble, clean, and regrease leaking stopcocks. Replace leaking rubber connections. After the analyzer is reassembled, repeat the leak-check procedure.

## 7. CALCULATIONS

### 7.1 *Nomenclature*

S?

$M[d]$  = Dry molecular weight, g/g-mole (lb/lb-mole).

%CO<sub>2</sub> = Percent CO<sub>2</sub> by volume, dry basis.

%O<sub>2</sub> = Percent O<sub>2</sub> by volume, dry basis.

%CO = Percent CO by volume, dry basis.

%N<sub>2</sub> = Percent N<sub>2</sub> by volume, dry basis.

0.280 = Molecular weight of N<sub>2</sub> or CO, divided by 100.

0.320 = Molecular weight of O<sub>2</sub> divided by 100.

0.440 = Molecular weight of CO<sub>2</sub> divided by 100.

7.2 Dry Molecular Weight. Use Equation 3-1 to calculate the dry molecular weight of the stack gas.

$$M[d] = 0.440(\%CO_2) + 0.320 (\%O_2) + 0.280(\%N_2 + \%CO)$$

Eq. 3-1

NOTE. The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. The tester may choose to include argon in the analysis using procedures subject to approval of the Administrator.

## 8. BIBLIOGRAPHY

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### METHOD 3A -- DETERMINATION OF OXYGEN AND CARBON DIOXIDE CONCENTRATIONS IN EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

#### 1. *Applicability and Principle*

1.1 *Applicability.* This method is applicable to the determination of oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) concentrations in emissions from stationary sources only when specified within the regulations.

1.2 *Principle.* A sample is continuously extracted from the effluent stream: a portion of the sample stream is conveyed to an instrumental analyzer(s) for determination of O<sub>2</sub> and CO<sub>2</sub> concentration(s). Performance specifications and test procedures are provided to ensure reliable data.

#### 2. *Range and Sensitivity*

Same as Method 6C, Sections 2.1 and 2.2, except that the span of the monitoring system shall be selected such that the average O<sub>2</sub> or CO<sub>2</sub> concentration is not less than 20 percent of the span.

#### 3. *Definitions*

3.1 *Measurement System.* The total equipment required for the determination of the O<sub>2</sub> or CO<sub>2</sub> concentration. The measurement system consists of the same major subsystems as defined in Method 6C,

Sections 3.1.1, 3.1.2, and 3.1.3.

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, Response Time, and Calibration Curve. Same as Method 6C, Sections 3.2 through 3.8, and 3.10.

3.3 Interference Response. The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

#### 4. *Measurement System Performance Specifications*

Same as Method 6C, Sections 4.1 through 4.4.

#### 5. *Apparatus and Reagents*

5.1 Measurement System. Any measurement system for O<sub>2</sub> or CO<sub>2</sub> that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1 of Method 6C. The essential components of the measurement system are described below:

5.1.1 Sample Probe. A leak-free probe, of sufficient length to traverse the sample points.

5.1.2 Sample Line. Tubing, to transport the sample gas from the probe to the moisture removal system. A heated sample line is not required for systems that measure the O<sub>2</sub> or CO<sub>2</sub> concentration on a dry basis, or transport dry gases.

5.1.3 Sample Transport Line, Calibration Value Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder. Same as Method 6C, Sections 5.1.3 through 5.1.9, and 5.1.11, except that the requirements to use stainless steel, Teflon, and nonreactive glass filters do not apply.

5.1.4 Gas Analyzer. An analyzer to determine continuously the O<sub>2</sub> or CO<sub>2</sub> concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate the analyzer is insensitive to flow variations over the range encountered during the test.

5.2 Calibration Gases. The calibration gases for CO<sub>2</sub> analyzers shall be CO<sub>2</sub> in N<sub>2</sub> or CO<sub>2</sub> in air. Alternatively, CO<sub>2</sub> /SO<sub>2</sub>, O<sub>2</sub>/SO<sub>2</sub>, or O<sub>2</sub> /CO<sub>2</sub> /SO<sub>2</sub> gas mixtures in N<sub>2</sub> may be used. Three calibration gases, as specified Section 5.3.1 through 5.3.3 of Method 6C, shall be used. For O<sub>2</sub> monitors that cannot analyze zero gas, a calibration gas concentration equivalent to less than 10 percent of the span may be used in place of zero gas.

#### 6. *Measurement System Performance Test Procedures*

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Concentration Verification. Follow Section 6.1 of Method 6C, except if calibration gas analysis is required, use Method 3 and change the acceptance criteria for agreement among Method 3 results to 5 percent (or 0.2 percent by volume, whichever is greater).

6.2 Interference Response. Conduct an interference response test of the analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter

the interference response (e.g., changes in the type of gas detector). Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sampling System Bias Check. Follow Sections 6.2 through 6.4 of Method 6C.

### 7. *Emission Test Procedure*

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 3.

7.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., +/- 10 percent) during the entire run. The sampling time per run shall be the same as for tests conducted using Method 3 plus twice the system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed to determine the average effluent concentration.

7.3 Zero and Calibration Drift Test. Follow Section 7.4 of Method 6C.

### 8. *Quality Control Procedures*

The following quality control procedures are recommended when the results of this method are used for an emission rate correction factor, or excess air determination. The tester should select one of the following options for validating measurement results:

8.1 If both O<sub>2</sub> and CO<sub>2</sub> are measured using Method 3A, the procedures described in Section 4.4 of Method 3 should be followed to validate the O<sub>2</sub> and CO<sub>2</sub> measurement results.

8.2 If only O<sub>2</sub> is measured using Method 3A, measurements of the sample stream CO<sub>2</sub> concentration should be obtained at the sample by-pass vent discharge using an Orsat or Fyrite analyzer, or equivalent. Duplicate samples should be obtained concurrent with at least one run. Average the duplicate Orsat or Fyrite analysis results for each run. Use the average CO<sub>2</sub> values for comparison with the O<sub>2</sub> measurements in accordance with the procedures described in Section 4.4 of Method 3.

8.3 If only CO<sub>2</sub> is measured using Method 3A, concurrent measurements of the sample stream CO<sub>2</sub> concentration should be obtained using an Orsat or Fyrite analyzer as described in Section 8.2. For each run, differences greater than 0.5 percent between the Method 3A results and the average of the duplicate Fyrite analysis should be investigated.

### 9. *Emission Calculation*

For all CO<sub>2</sub> analyzers, and for O<sub>2</sub> analyzers that can be calibrated with zero gas, follow Section 8 of Method 6C, except express all concentrations as percent, rather than ppm.

For O<sub>2</sub> analyzers that use a low-level calibration gas in place of a zero gas, calculate the effluent gas concentration using Equation 3A-1.

$$C[\text{gas}] = C[\text{ma}] - C[\text{oa}] / C[\text{m}] - C[\text{o}] (C - C[\text{m}]) + C[\text{ma}]$$

Eq. 3A-1

Where:

C[*gas*] = Effluent gas concentration, dry basis, percent.

C[*ma*] = Actual concentration of the upscale calibration gas, percent.

C[*oa*] = Actual concentration of the low-level calibration gas, percent.

C[*m*] = Average of initial and final system calibration bias check responses for the upscale calibration gas, percent.

C[*o*] = Average of initial and final system calibration bias check responses for the low-level gas, percent.

C = Average gas concentration indicated by the gas analyzer, dry basis, percent.

## 10. Bibliography

Same as bibliography of Method 6C.

## METHOD 3B -- GAS ANALYSIS FOR THE DETERMINATION OF EMISSION RATE CORRECTION FACTOR OR EXCESS AIR

### 1. APPLICABILITY AND PRINCIPLE

#### 1.1 Applicability

1.1.1 This method is applicable for determining carbon dioxide (CO[2] ), oxygen (O[2] ), and carbon monoxide (CO) concentrations of a sample from a gas stream of a fossil-fuel combustion process for excess air or emission rate correction factor calculations.

1.1.2 Other methods, as well as modifications to the procedure described herein, are also applicable for 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, and (2) a method using CO[2] or O[2] and stoichiometric calculations to determine excess air. These methods and modifications may be used, but are subject to the approval of the Administrator, U.S. Environmental Protection Agency (EPA).

1.1.3 Note. Mention of trade names or specific products does not constitute endorsement by EPA.

1.2 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 CO[2] percent O[2], and, if necessary, percent CO. An Orsat analyzer must be used for excess air or emission rate correction factor determinations.

### 2. APPARATUS

The alternative sampling systems are the same as those mentioned in Section 2 of Method 3.

2.1 Grab Sampling and Integrated Sampling. Same as in Sections 2.1 and 2.2, respectively, of Method 3.

2.2 Analysis. An Orsat analyzer only. For low CO[2] (less than 4.0 percent) or high O[2] (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions. For Orsat maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless

otherwise specified herein.

### 3. PROCEDURES

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.

NOTE. -- A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determinations, unless approved by the Administrator. If both percent CO<sub>2</sub> and percent O<sub>2</sub> are measured, the analytical results of any of the three procedures given below may be used for calculating the dry molecular weight (see Method 3).

#### *3.1 Single-Point, Grab Sampling and Analytical Procedure.*

3.1.1 The sampling point in the duct shall be as described in Section 3.1 of Method 3.

3.1.2 Set up the equipment as shown in Figure 3-1 of Method 3, making sure all connections ahead of the analyzer are tight. Leak check the Orsat analyzer according to the procedure described in Section 6 of Method 3. This leak check is mandatory.

3.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer. For emission rate correction factor determinations, immediately analyze the sample, as outlined in Sections 3.1.4 and 3.1.5, for percent CO<sub>2</sub> or percent O<sub>2</sub>. If excess air is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 3.1.4 and 3.1.5, for percent CO<sub>2</sub>, O<sub>2</sub>, and CO; (2) determine the percentage of the gas that is N<sub>2</sub> by subtracting the sum of the percent CO<sub>2</sub>, percent O<sub>2</sub>, and percent CO from 100 percent, and (3) calculate percent excess air as outlined in Section 4.2.

3.1.4 To ensure complete absorption of the CO<sub>2</sub>, O<sub>2</sub>, 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.)

NOTE. -- Since this single-point, grab sampling and analytical procedure is 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<sub>2</sub> or O<sub>2</sub> is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> be measured, and that Section 3.4 be used to validate the analytical data.

3.1.5 After the analysis is completed, leak check (mandatory) the Orsat analyzer once again, as described in Section 6 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.

#### *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 (mandatory) the flexible bag as in Section 2.2.6 of Method 3. Set up the equipment as shown in Figure 3-2 of Method 3. Just before sampling, leak check (mandatory) the train as described in Section 4.2 of Method 3.

3.2.3 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<sup>3</sup>) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

3.2.4 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<sub>2</sub> or percent O<sub>2</sub> (as outlined in Sections 3.2.5 through 3.2.7). The Orsat analyzer must be leak checked (see Section 6 of Method 3) 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 3.2.5 through 3.2.7) for percent CO<sub>2</sub>, O<sub>2</sub>, and CO; (2) determine the percentage of the gas that is N<sub>2</sub> by subtracting the sum of the percent CO<sub>2</sub>, percent O<sub>2</sub>, and percent CO from 100 percent; and (3) calculate percent excess air, as outlined in Section 4.2.

3.2.5 To ensure complete absorption of the CO<sub>2</sub>, O<sub>2</sub>, or if applicable, CO, follow the procedure described in Section 3.1.4.

NOTE. -- Although in most instances only CO<sub>2</sub> or O<sub>2</sub> is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> be measured, and that Section 3.4.1 be used to validate the analytical data.

3.2.6 Repeat the analysis until the following criteria are met:

3.2.6.1 For percent CO<sub>2</sub>, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO<sub>2</sub> is greater than 4.0 percent or (b) 0.2 percent by volume when CO<sub>2</sub> is less than or equal to 4.0 percent. Average three acceptable values of percent CO<sub>2</sub>, and report the results to the nearest 0.2 percent.

3.2.6.2 For percent O<sub>2</sub>, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O<sub>2</sub> is less than 15.0 percent or (b) 0.2 percent by volume when O<sub>2</sub> is greater than or equal to 15.0 percent. Average the three acceptable values of percent O<sub>2</sub>, and report the results to the nearest 0.1 percent.

3.2.6.3 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.

3.2.7 After the analysis is completed, leak check (mandatory) the Orsat analyzer once again, as described in Section 6 of Method 3. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.

### *3.3 Multi-Point, Integrated Sampling and Analytical Procedure.*

3.3.1 The sampling points shall be determined as specified in Section 5.3 of Method 3.

3.3.2 Follow the procedures outlined in Sections 3.2.2 through 3.2.7, 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 of Method 3.

### *3.4 Quality Control Procedures.*

3.4.1 Data Validation When Both CO<sub>2</sub> and O<sub>2</sub> Are Measured. Although in most instances, only CO<sub>2</sub> or O<sub>2</sub> measurement is required, it is recommended that both CO<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub> or O<sub>2</sub> through processes other than combustion, (2) add O<sub>2</sub> (e.g., oxygen enrichment) and N<sub>2</sub> in proportions different from that of air, (3) add CO<sub>2</sub> (e.g., cement or lime kilns), or (4) have no fuel factor, F<sub>o</sub>, values obtainable (e.g., extremely variable waste mixtures). This method validates the measured proportions of CO<sub>2</sub> and O<sub>2</sub> for 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<sub>2</sub> added or removed from the gas stream is not significant in relation to the total CO<sub>2</sub> concentration. The CO<sub>2</sub> concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F<sub>o</sub> check minimally useful.

3.4.1.1 Calculate a fuel factor, F<sub>o</sub>, using the following equation:

$$F_o = 20.9 - \%O_2 / \%CO_2$$

Eq. 3B-1

where:

%O<sub>2</sub> = Percent O<sub>2</sub> by volume, dry basis.

%CO<sub>2</sub> = Percent CO<sub>2</sub> by volume, dry basis.

20.9 = Percent O<sub>2</sub> by volume in ambient air.

If CO present in quantities measurable by this method, adjust the O<sub>2</sub> and CO<sub>2</sub> values before performing the calculation for F<sub>o</sub> as follows:

$$\%CO_2 \text{ (adj)} = \%CO_2 + \%CO$$

$$O_2 \text{ (adj)} = \%O_2 - 0.5 \%CO$$

where:

%5CO = Percent CO by volume, dry basis.

3.4.1.2 Compare the calculated F<sub>o</sub> factor with the expected F<sub>o</sub> values. The following table may be used in establishing acceptable ranges for the expected F<sub>o</sub> if the fuel being burned is known. When fuels are burned in combinations, calculate the combined fuel F<sub>d</sub> and F<sub>c</sub> factors (as defined in Method 19) according to the procedure in Method 19, Section 5.2.3. Then calculate the F<sub>o</sub> factor as follows:

$$F_o = 0.209 F_d / F_c$$

Eq. 3B-2

Fuel type	F <sub>o</sub> 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

3.4.1.3 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.

#### 4. CALCULATIONS

4.1 Nomenclature. Same as Section 5 of Method 3 with the addition of the following:

%EA = Percent excess air.

0.264 = Ratio of O[2] to N[2] in air, v/v.

4.2 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 3.1.3 or 3.2.4) into Equation 3B-3.

$$\%EA = \%O[2] - 0.5 \%CO / 0.264 \%N[2] - (\%O[2] - 0.5 \%CO) \times 100$$

Eq. 3B-3

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, alternative methods, subject to approval of the Administrator, are required.

#### 5. BIBLIOGRAPHY

Same as Method 3.

#### METHOD 4 -- DETERMINATION OF MOISTURE CONTENT IN STACK GASES

##### 1. Principle and Applicability

1.1 Principle. A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

1.2 Applicability. This method is applicable for determining the moisture content of stack gas.

Two procedures are given. The first is a reference method, for accurate determinations of moisture content (such as are needed to calculate emission data). The second is an approximation method, which provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content, e.g., drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc., are also acceptable.

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, U.S. Environmental Protection Agency, to be capable of yielding results within 1 percent H<sub>2</sub>O of the reference method.

NOTE: The reference method may yield questionable results when applied to saturated gas streams or to streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to +/- 1 deg. C (2 deg. F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternative methods, subject to the approval of the Administrator, shall be used.

## *2. Reference Method*

The procedure described in Method 5 for determining moisture content is acceptable as a reference method.

2.1 Apparatus. A schematic of the sampling train used in this reference method is shown in Figure 4-1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.

Figure 4-1. Moisture sampling train-reference method.

[SEE FIGURE IN ORIGINAL]

2.1.1 Probe. The probe is constructed of stainless steel or glass tubing, sufficiently heated to prevent water condensation, and is equipped with a filter, either in-stack (e.g., a plug of glass wool inserted into the end of the probe) or heated out-stack (e.g., as described in Method 5), to remove particular matter.

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

2.1.2 Condenser. The condenser consists of four impingers connected in series with ground glass, leak-free fittings or any similarly leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 centimeter (1/2 inch) ID glass tube extending to about 1.3 cm (1/2 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 two impingers shall contain known volumes of water, the third shall be empty, and the fourth shall contain a known weight of 6- to 16-mesh indicating type silica gel, or equivalent desiccant. If the silica gel has been previously used, dry at 175 deg. C (350 deg. F) for 2 hours. New silica gel may be used as received. A thermometer, capable of measuring temperature to within 1 deg. C (2 deg. F), shall be placed at the outlet of the fourth impinger, for monitoring purposes.

Alternatively, any system may be used (subject to the approval of the Administrator) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. 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 gas stream through a tared silica gel (or equivalent desiccant) trap, with exit gases kept below 20 deg. C (68 deg. 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.

2.1.3 Cooling System. An ice bath container and crushed ice (or equivalent) are used to aid in condensing moisture.

2.1.4 Metering System. This system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3 deg. C (5.4 deg. F), dry gas meter capable of measuring volume to within 2 percent, and related equipment as shown in Figure 4-1. Other metering systems, capable of maintaining a constant sampling rate and determining sample gas volume, may be used, subject to the approval of the Administrator.

2.1.5 Barometer. 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 Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.6 Graduated Cylinder and/or Balance. These items are used to measure condensed water and moisture caught in the silica gel to within 1 ml or 0.5 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. These balances are suitable for use here.

2.2 Procedure. The following procedure is written for a condenser system (such as the impinger system described in Section 2.1.2) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 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 points 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 in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. 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. Place known volumes

of water in the first two impingers. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

2.2.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m<sup>3</sup>/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

2.2.3 Set up the sampling train as shown in Figure 4-1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of about 120 deg. C (248 deg. F), to prevent water condensation ahead of the condenser; allow time for the temperatures to stabilize. Place crushed ice in the ice bath container. It is recommended, but not required, that a leak check be done, as follows: Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder) and pull a 380 mm (15 in.) Hg vacuum; a lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m<sup>3</sup>/min (0.02 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

2.2.4 During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

2.2.5 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less 20 deg. C (68 deg. F) at the silica gel outlet.

2.2.6 After collecting the sample, disconnect the probe from the filter holder (or from the first impinger) and conduct a leak check (mandatory) as described in Section 2.2.3. Record the leak rate. If the leakage rate exceeds the allowable rate, the tester shall either reject the test results or shall correct the sample volume as in Section 6.3 of Method 5. Next, measure the volume of the moisture condensed to the nearest ml. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4-3) and calculate the moisture percentage, as described in 2.3 below.

2.2.7 A quality control check of the volume metering system at the field site is suggested before collecting the sample following the procedure in Method 5, Section 4.4

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

## FIGURE 4-2 -- FIELD MOISTURE DETERMINATION REFERENCE METHOD

[SEE FIGURE IN ORIGINAL]

## FIGURE 4-3 -- ANALYTICAL DATA -- REFERENCE METHOD

	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Difference		

### 2.3.1 Nomenclature.

B[ws] = Proportion of water vapor, by volume, in the gas stream.

M[w] = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P[m] = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, 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<sup>3</sup> / (g-mole) (deg. K) for metric units and 21.85 (in. Hg) (ft<sup>3</sup> / (lb-mole) (deg. R) for English units.

T[m] = Absolute temperature at meter, deg. K ( deg. R).

T[std] = Standard absolute temperature, 293 deg. K (528 deg. R).

V[m] = Dry gas volume measured by dry gas meter, dcm (dcf).

DELTA V[m] = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

V[m(std)] = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V[wc(std)] = Volume of water vapor condensed corrected to standard conditions, scm (scf).

V[wsg(std)] = Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).

V[f] = Final volume of condenser water, ml.

V[i] = Initial volume, if any, of condenser water, ml.

W[f] = Final weight of silica gel or silica gel plus impinger, g.

W[i] = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

$\rho[w]$  = Density of water, 0.9982 g/ml (0.002201 lb / ml).

### 2.3.2 Volume of Water Vapor Condensed.

$$V[wc(std)] = (V[f] - V[i] \rho[w] RT[std] / P[std] M[w] = K[1] (V[f] - V[i])$$

Eq. 4-1

Where:

$$K[1] = 0.001333 \text{ m}^3 / \text{ml for metric units} = 0.04707 \text{ ft}^3 / \text{ml for English units}$$

### 2.3.3 Volume of Water Vapor Collected in Silica Gel.

$$V[wsg(std)] = (W[f] - W[i]) RT[std] / P[std] M[w] = K[2] (W[f] - W[i])$$

Eq. 4-2

Where:

$$K[2] = 0.001335 \text{ m}^3 / \text{g for metric units} = 0.04715 \text{ ft}^3 / \text{g for English units}$$

### 2.3.4 Sample Gas Volume.

$$V[m(std)] = V[m] Y (P[m]) (T[std]) / (P[std]) (T[m]) = K[3] Y V[m] P[m] / T[m]$$

Eq. 4-3

Where:

$$K[3] = 0.3858 \text{ deg. K/mm Hg for metric units} = 17.64 \text{ deg. R/in. Hg for English units}$$

Note: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of  $V[m]$  in Equation 4-3, as described in Section 6.3 of Method 5.

### 2.3.5 Moisture Content.

$$B[ws] = V[wc(std)] + V[wsg(std)] / V[wc(std)] + V[wsg(std)] + wsg(std)] = V[m(std)]$$

Eq. 4-4

NOTE: In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see Section 1.2), and another based upon the results of the impinger analysis. The lower of these two values of  $B[ws]$  shall be considered correct.

2.3.6 Verification of Constant Sampling Rate. For each time increment, determine the DELTA  $V[m]$ . Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

## 3. Approximation Method

The approximation method described below is presented only as a suggested method (see Section 1.2).

### 3.1 Apparatus.

3.1.1 Probe. Stainless steel glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter. A plug of glass wool, inserted into the end of the probe, is a satisfactory filter.

3.1.2 Impingers. Two midjet impingers, each with 30 ml capacity, or equivalent.

3.1.3 Ice Bath. Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

3.1.5 Valve. Needle valve, to regulate the sample gas flow rate.

3.1.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

3.1.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2%, and calibrated over the range of flow rates and conditions actually encountered during sampling.

3.1.8 Rate Meter. Rotameter, to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated Cylinder. 25 ml.

3.1.10 Barometer. Mercury, aneroid, or other barometer, as described in Section 2.1.5 above.

3.1.11 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

### 3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger.

Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in. Hg). Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0-40 cc/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plus before turning off the pump.

Figure 4-4. Moisture sampling train - approximation method.

[SEE FIGURE IN ORIGINAL]

FIGURE 4-5 -- FIELD MOISTURE DETERMINATION -- APPROXIMATION METHOD

	Location	Comments:
	Test	
	Date	
	Operator	
	Barometric pressure	
	<b>Gas volume</b>	<b>Rate meter</b>
	<b>through</b>	<b>setting m</b>
	<b>meter,</b>	<b>&lt;3&gt; /</b>
<b>Clock</b>	<b>(V[m]),</b>	<b>min (ft &lt;3&gt;</b>
<b>time</b>	<b>m&lt;3&gt;</b>	<b>/</b>
	<b>(ft&lt;3&gt;)</b>	<b>min)</b>
		<b>Meter</b>
		<b>deg. C (deg. F)</b>

3.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft <3>) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure the volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content, for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B[wm] = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.

B[ws] = Water vapor in the gas stream, proportion by volume.

M[w] = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P[m] = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.

P[std] = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m <3>) / (g-mole) (deg. K) for metric units and 21.85 (in. Hg) (ft <3>) / lb-mole) (deg. R) for English units.

T[m] = Absolute temperature at meter, deg. K ( deg. R).

T[std] = Standard absolute temperature, 293 deg. K (528 deg. R).

V[f] = Final volume of impinger contents, ml.

V[i] = Initial volume of impinger contents, ml.

V[m] = Dry gas volume measured by dry gas meter, dcm (dcf).

V[m(std)] = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

V[wc(std)] = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

rho[w] = Density of water, 0.9982 g/ml (0.002201 lb/ml).

Y = Dry gas meter calibration factor.

### 3.3.2 Volume of Water Vapor Collected.

$$V[wc] = (V[f] - V[i]) \rho[w] RT[std] / P[std] M[w] = K[1] (V[f] - V[i])$$

Eq. 4-5

Where:

$$K[1] = 0.001333 \text{ m}^3 / \text{ml} \text{ for metric units} = 0.04707 \text{ ft}^3 / \text{ml} \text{ for English units.}$$

### 3.3.3 Gas Volume.

$$V[m(std)] = V[m] (P[m] / P[std]) (T[std]) / T[m] = K[2] V[m] P[m] / T[m]$$

Equation 4-6

where:

$$K[2] = 0.3858 \text{ deg. K/mm Hg for metric units} = 17.64 \text{ deg. R/in. Hg for English units}$$

### 3.3.4 Approximate Moisture Content.

$$B[ws] = V[wc] / V[wc] + V[m(std)] + B[wm] = V[wc] / V[wc] + V[m(std)] + (0.025)$$

Equation 4-7

## 4. Calibration

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); and Section 5.7 (barometer). The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the approximation method, use the procedures outlined in Section 5.1.1 of Method 6 to calibrate the metering system, and the procedure of Method 5, Section 5.7 to calibrate the barometer.

## 5. Bibliography

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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 deg. C (248 +/- 25 deg. 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:

Figure 5-1. Particulate-sampling train.

[SEE FIGURE IN ORIGINAL]

2.1.1 Probe Nozzle, Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be  $\leq 30$  deg. 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 (1/8 to 1/2 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 deg. C (248 +/- 25 deg. 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 deg. C (900 deg. F); quartz liners shall be used for temperatures between 480 and 900 deg. C (900 and 1,650 deg. 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 deg. C (1,508 deg. F), and for quartz it is 1,500 deg. C (2,732 deg. 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, n2 or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

n2 Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

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.

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 for velocity head ( $\Delta \rho$ ) 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, if used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 +/- 14 deg C (248 +/- 25 deg. 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 deg. C (5.4 deg 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 (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 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 temperature to within 1 deg. C (2 deg. 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 gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20 deg. C (68 deg. 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 deg. C (5.4 deg. 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 described 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 rubberbacked 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 for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Airtight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

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

2.3 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 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 deg. C (350 deg. 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, deionized 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.

3.2 Sample Recovery. Acetone-reagent grade,  $\leq 0.001$  percent residue, in glass bottles -- is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values ( $\leq 0.001$  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 procedure 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  $20 \pm 5.6$  deg. C ( $68 \pm 10$  deg. 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 deg. C (200 deg. 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 deg. C (500 deg. 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 (cyclone, 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<sup>3</sup>/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 valve; 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 necessary, 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<sup>3</sup>/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 leak-check 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<sup>3</sup>/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 deg. C (248 +/- 25 deg. 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.

#### FIGURE 5-2 -- PARTICULATE FIELD DATA

[SEE FIGURE IN ORIGINAL]

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 off the openings around the probe and porthole to prevent unrepresentative dilution of the 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 walls when sampling near the walls or when removing or inserting the probe through the portholes; 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 deg. C (68 deg. 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.

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 occurred 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 gain
1			
2			
Total			
Less acetone blank			
Weight of particulate matter			

	Volume of liquid water collected	
	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 weight increase by density of water (1 g/ml).

Increase, g / (1 g/ml) = 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 deg. C (220 deg. 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 deg. C (220 deg. 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 volumetrically 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[at] for the metering system orifice. The DELTA H[at] is the orifice pressure differential in units of in. H<sub>2</sub>O that correlates to 0.75 cfm of air at 528 deg. R and 29.92 in. Hg. The DELTA H[at] is calculated as follows:

$$\text{DELTA H[at]} = 0.0319 \text{ DELTA H T[m]} / \text{P[bar]} \text{ circle minus } \langle 2 \rangle / \text{Y} \langle 2 \rangle \text{ V} \langle 2 \rangle \text{[m]}$$

Eq. 5-9

Where:

DELTA H = Average pressure differential across the orifice meter, in. H<sub>2</sub>O.

T[m] = Absolute average dry gas meter temperature, deg. R.

P[bar] = Barometric pressure, in. Hg.

circle minus = 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 in. Hg/ deg. R) x (0.75 cfm)<sup>2</sup>.

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[at] 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:

$$Y[c] = 10 / V[m] [0.0319 T[m] / P [bar]]^{1/2}$$

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.

SOURCE: [36 FR 24877, Dec. 23, 1971]

AUTHORITY: 42 U.S.C. 7401, 7411, 7414, 7416, and 7601.

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

§ 60. Appendix A to Part 60 -- Test Methods [PART II OF VII]

**40 CFR 60. Appendix A to Part 60**

*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 0.025 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 ft<sup>3</sup>/rev). A spirometer of 400 liters (14 ft<sup>3</sup>) 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 m<sup>3</sup> (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[at], the orifice calibration factor, at each orifice setting as shown on Figure 5.6. Allowable tolerances for individual Y and DELTA H[at], values are given in Figure 5.6. Use the average of the Y values in the calculations in Section 6.

[SEE FIGURE IN ORIGINAL]

[SEE FIGURE IN ORIGINAL]

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 0.00057m<sup>3</sup>/min

(0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m<sup>3</sup>/min (0.02 cfm).

5.3.2 Calibration After Use. After each field 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, insert 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 sample 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 following 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.

[SEE FIGURE IN ORIGINAL]

### 6.1 Nomenclature.

A[n] = Cross-sectional area of nozzle, m<sup>2</sup> (ft<sup>2</sup>).

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 0.00057 m<sup>3</sup>/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<sup>th</sup>" component change (i = 1, 2, 3, . . . n), m<sup>3</sup>/min (cfm).

L[p] = Leakage rate observed during the post-test leak check, m<sup>3</sup>/min (cfm).

m[a] = Mass of residue of acetone after evaporation, mg.

m[n] = Total amount of particulate matter collected, mg.

M[w] = Molecular weight of water, 18.0 g/g-mole (18.0lb/lb-mole).

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<sup>3</sup>/deg. K-g-mole (21.85 in. Hg-ft<sup>3</sup>/deg. R-lb-mole).

T[m] = Absolute average dry gas meter temperature (see Figure 5-2), deg. K (deg. R).

T[s] = Absolute average stack gas temperature (see Figure 5-2), deg. K (deg. R).

T[std] = Standard absolute temperature, 293 deg. K (528 deg. R).

V[a] = Volume of acetone blank, ml.

V[aw] = Volume of acetone used in wash, ml.

V[ic] = 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.

DELTA H = Average pressure differential across the orifice meter (see Figure 5-2), mm H<sub>2</sub>O (in. H<sub>2</sub>O).

rho[a] = Density of acetone, mg/ml (see label on bottle).

rho[w] = Density of water, 0.9982 g/ml (0.002201 lb/ml).

THETA - Total sampling time, min.

THETA[1] = Sampling time interval, from the beginning of a run until the first component change, min.

THETA[i] = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

THETA[p] = Sampling time interval, from the final (n<sup>th</sup>) 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 deg. C, 760 mm Hg or 68 deg. F, 29.92 in. Hg) by using Equation 5-1.

$$V[m(\text{std})] = V[m] Y \left( \frac{T[\text{std}]}{T[m]} \right) \left[ \frac{P[\text{bar}] + \text{DELTA H}}{13.6 P[\text{std}]} \right] = K[1] V[m] Y \left[ \frac{P[\text{bar}] + (\text{DELTA H} / 13.6)}{P[\text{std}]} \right]$$

Equation 5-1

Where;

K[1] = 0.3858 deg. K/mm Hg for metric units = 17.64 deg. 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 posttest leak check or leak checks conducted prior to component changes) exceeds L[a]. If L[p] or [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:

$$[V[m] - (L[p] - L[a])\text{THETA}]$$

(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:

$$V[m] - (L[i] - L[a]) \text{ THETA}[1] - \langle N \rangle \text{ SIGMA } [i=2] (L[p] - L[a]) \text{ THETA}[11]$$

and substitute only for those leakage rates (L[i] or L[p]) which exceed L[a].

#### 6.4 Volume of Water Vapor.

$$V[w(\text{std})] = V[1c] \text{ RHO } [w] \text{ R } T[\text{std}] / M[w] \text{ P}[\text{std}] = K[2] V[1c]$$

Eq. 5-2

Where:

$$K[2] = 0.001333 \text{ m}^3 / \text{ml for metric units}$$

$$= 0.04707 \text{ ft}^3 / \text{ml for English units.}$$

#### 6.5 Moisture Content.

$$B[ws] = V[w(\text{std})] / V[m(\text{std}) + V[w(\text{std})]$$

Eq. 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 deg. C (2 deg. F).

#### 6.6 Acetone Blank Concentration.

$$C[a] = m[a] / V[a \text{ rho } a]$$

Eq. 5-4

#### 6.7 Acetone Wash Blank.

$$W[a] = C[a] V[aw \text{ rho } a]$$

Eq. 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.

$$c[s] = (0.001 \text{ g/mg}) (m[n] / V[m(\text{std})])$$

Eq. 5-6

#### 6.10 Conversion Factors:

From	To	Multiply by
scf	m <sup>3</sup>	0.02832.
g	mg	0.001
g/ft <sup>3</sup>	gr/ft <sup>3</sup>	15.43.
g/ft <sup>3</sup>	lb/ft <sup>3</sup>	2.205 X 10 <sup>-3</sup> .
g/ft <sup>3</sup>	g/m <sup>3</sup>	35.31.

#### 6.11 Isokinetic Variation.

##### 6.11.1 Calculation From Raw Data.

$$I = 100 T[s][K[3] V[1c] + (V[m] Y/T[m])(P[\text{bar}] + \text{DELTA } H/13.6)] / 60 \text{ THETA } V[s] P[s] A[n]$$

Eq. 5-7

Where:

$$K[3] = 0.003454 \text{ mm Hg} - \text{m}^3/\text{ml} - \text{deg. K for metric units.}$$

$$= 0.002669\text{-in. Hg} - \text{ft}^3/\text{ml} - \text{deg. R for English units.}$$

##### 6.11.2 Calculation From Intermediate Values.

$$I = 100 T[s] V[m(\text{std})] P[\text{std}] / 60 T[\text{std}] V[s] \text{ THETA } A[n] P[s] (1 - B[\text{ws}])$$

$$= K[4] T[s] V[m(\text{std})] / P[s] V[s] A[n] \text{ THETA } (1 - B[\text{ws}])$$

Eq. 5-8

Where:

$$K[4] = 4.320 \text{ for metric units}$$

$$= 0.09450 \text{ for English units.}$$

6.12 Acceptable Results. If 90 percent  $\leq I \leq$  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 judged 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 ft<sup>3</sup>/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 ft<sup>3</sup>/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 H<sub>2</sub>O (4 in. H<sub>2</sub>O) at a flow rate of 30 liters/min (1 cfm)]. This can be accomplished by using large diameter tubing connections and straight pipe fittings.

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.

[SEE FIGURE IN ORIGINAL]

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

[SEE FIGURE IN ORIGINAL]

7.1.1.4 Calculate flow rate, Q, for each run using the wet test meter gas volume, V[w], and the run time, THETA. Calculate the dry gas meter coefficient, Y[ds], for each run. These calculations are as follows:

$$Q = K[1] P[\text{bar}] / t[\text{w}] + t[\text{std}] \times V[\text{w}] / \text{THETA}$$

$$Y[\text{ds}] = V[\text{w}] / V[\text{ds}] \times (t[\text{ds}] + t[\text{std}]) / (t[\text{w}] + t[\text{std}]) \times P[\text{bar}] / (P[\text{bar}] + \text{DELTA } p / 13.6)$$

Where:

K[1] = 0.3858 for international system of units (SI); 17.64 for English units.

V[w] = Wet test meter volume, liters (ft<sup>3</sup>).

V[ds] = Dry gas meter volume, liters (ft<sup>3</sup>).

t[ds] = Average dry gas meter temperature, deg. C ( deg. F).

$t[\text{std}] = 273 \text{ deg. C for SI units; } 460 \text{ deg. F for English units.}$

$t[\text{w}] = \text{Average wet test meter temperature, deg. C (deg. F).}$

$P[\text{bar}] = \text{Barometric pressure, mm Hg (in. Hg).}$

$\text{DELTA } p = \text{Dry gas meter inlet differential pressure, mm H}_2\text{O (in. H}_2\text{O).}$

$\text{THETA} = \text{Run time, min.}$

7.1.1.5 Compare the three  $Y[\text{ds}]$  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  $Y[\text{ds}]$  values at each flow rate resulting in five average meter coefficients,  $Y[\text{ds}]$ .

7.1.1.6 Prepare a curve of meter coefficient,  $Y[\text{ds}]$ , 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  $\pm 1.5$  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:

	Flow rate		Flow rate
Gauge/cm	(liters/min)	Gauge/cm	(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 1/2-inch Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9.

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

[SEE FIGURE IN ORIGINAL]

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 turn 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.

[SEE FIGURE IN ORIGINAL]

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 m<sup>3</sup> (0.1 ft<sup>3</sup>) 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.

$$K' = K[1]V[m]Y (P[bar] + \Delta H/13.6) \sqrt{T[amb]} / P[bar] T[m] \text{ circle minus}$$

Eq. 5-9

Where:

K' = Critical orifice coefficient,

root T[amb] = Absolute ambient temperature, deg. K ( deg. 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	m <sup>3</sup> (ft <sup>3</sup> )	
Initial reading	m <sup>3</sup> (ft <sup>3</sup> )	
Difference, V[m]	m <sup>3</sup> (ft <sup>3</sup> )	
Inlet/Outlet temperatures:		
Initial	deg. C ( deg. F)	/ /
Final	deg. C ( deg. F)	/ /
Avg. Temperature, t[m]	deg. C (deg. F)	

Time, circle minus	min/sec	/	/
	min		
Orifice man. rdg.,			
DELTA H	mm (in.)	H[2]O	
Bar. pressure,			
P[bar]	mm (in.)	Hg	
Ambient temperature, deg. C ( deg. F)			
t[amb]			
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:

$$(m^{3})(deg. K)^{1/2} / (mmg. Hg.) (min) \times [(ft^{3})(deg. R)^{1/2} / (in. Hg) (min)]$$

$$V[m](std) = K[1] V[m] P[bar] + (DELTA H/13.6) / T[m]$$

Eq. 5-10

$$V[cr](std) = K' P[bar] \text{ circle minus} / \text{root } T[amb]$$

Eq. 5-11

$$Y = V[cr(std)] / V[m(std)]$$

Eq. 5-12

where:

V[cr(std)] = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dsm<sup>3</sup>(dscf).

K[1] = 0.3858 deg. K/mm Hg for metric units

= 17.64 deg. 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	m<3> (ft<3>)		
Initial reading	m<3> (ft<3>)		
Difference, V[m]	m<3> (ft<3>)		
Inlet/outlet temperatures:			
Initial	deg. C ( deg. F)	/	/
Final	deg. C ( deg. F)	/	/
Avg. Temperature, t[m]	deg. C ( deg. F)		
Time, circle minus	min/sec	/	/
	min		
Orifice man. rdg., DELTA H	mm (in.)		
	H[2]O.		
Bar. pressure, P[bar]	mm (in.) Hg		
Ambient temperature, t[amb]	deg. C ( deg. 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 5A -- DETERMINATION OF PARTICULATE EMISSIONS FROM THE ASPHALT PROCESSING AND ASPHALT ROOFING INDUSTRY

### 1. *Applicability and Principle*

1.1 *Applicability*. This method applies to the determination of particulate emissions from asphalt roofing industry process saturators, blowing stills, and other sources as specified in the regulations.

1.2 *Principle*. Particulate matter is withdrawn isokinetically from the source and collected on a glass filter fiber maintained at a temperature of 42 deg. +/- 10 deg. C (108 deg. +/- 18 deg. F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

### 2. *Apparatus*

2.1 *Sampling Train*. The sampling train configuration is the same as shown in Figure 5-1 of Method 5. The sampling train consists of the following components:

2.1.1 *Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Holder, Condenser, Metering System, Barometer, and Gas Density Determination Equipment*. Same as Method 5, Sections 2.1.1, 2.1.3 to 2.1.5, and 2.1.7 to 2.1.10, respectively.

2.1.2 *Probe Liner*. Same as in Method 5, Section 2.1.2, with the note that at high stack gas temperatures (greater than 250 deg. C (480 deg. F)), water-cooled probes may be required to control the probe exit temperature to 42 deg. +/- 10 deg. C (108 +/- 18 deg. F).

2.1.3 *Precollector Cyclone*. Borosilicate glass following the construction details shown in Air Pollution Technical Document-0581, "Construction Details of Isokinetic Source-Sampling Equipment".

NOTE: The tester shall use the cyclone when the stack gas moisture is greater than 10 percent. The tester shall not use the pre-collector cyclone under other, less severe conditions.

2.1.4 Filter Heating System. Any heating (or cooling) system capable of maintaining a sample gas temperature at the exit end of the filter holder during sampling at 42 +/- 10 deg. C (108 +/- 18 deg. F). Install a temperature gauge capable of measuring temperature within 3 deg. C (5.4 deg. F) at the exit side of the filter holder so that the sensing tip of the temperature gauge is in direct contact with the sample gas, and the sample gas temperature can be regulated and monitored during sampling. The temperature gauge shall comply with the calibration specifications defined in Section 5. The tester may use systems other than the one shown in APTD-0581.

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

2.2.1 Probe-Liner and Probe-Nozzle Brushes, Graduated Cylinder and/or Balance, Plastic Storage Containers, and Funnel and Rubber Policeman. Same as Method 5, Sections 2.2.1, 2.2.5, 2.2.6, and 2.2.7, respectively.

2.2.2 Wash Bottles. Glass.

2.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, with rubber-backed Teflon screw cap liners or caps that are constructed so as to be leak-free and resistant to chemical attack by 1,1,1-trichloroethane (TCE), 500-ml or 1000-ml. (Narrow mouth glass bottles have been found to be less prone to leakage.)

2.2.4 Petri Dishes. Glass, unless otherwise specified by the Administrator.

2.2.5 Funnel. Glass.

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

2.3.1 Glass Weighing Dishes, Desiccator, Analytical Balance, Balance, Hygrometer, and Temperature Gauge. Same as Method 5, Sections 2.3.1 to 2.3.4, 2.3.6, and 2.3.7, respectively.

2.3.2 Beakers. Glass, 250-ml and 500-ml.

2.3.3 Separatory Funnel. 100-ml or greater.

### 3. *Reagents*

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

3.1.1. Filters, Silica Gel, and Crushed Ice. Same as Method 5, Sections 3.1.1, 3.1.2, and 3.1.4, respectively.

3.1.2 Stopcock Grease. TCE-insoluble, heat-stable grease (if needed). This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

3.2 Sample Recovery. Reagent grade 1,1,1-trichloroethane (TCE),  $\leq 0.001$  percent residue and stored in glass bottles, is required. Run TCE blanks prior to field use and use only TCE with low blank values ( $\leq 0.001$  percent). The tester shall in no case subtract a blank value of greater than 0.001 percent of the weight of TCE used from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 TCE. Same as 3.2.

3.3.2 Desiccant. Same as Method 5, Section 3.3.2.

## 4. Procedure

4.1 Sampling Train Operation. The complexity of this method is such that in order to obtain reliable results, testers should be trained and experienced with Method 5 test procedures.

4.1.1 Pretest Preparation. Unless otherwise specified, maintain and calibrate all components according to the procedure described in Air Pollution Technical Document-0576, "Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment".

Prepare probe liners and sampling nozzles as needed for use. Thoroughly clean each component with soap and water followed by a minimum of three TCE rinses. Use the probe and nozzle brushes during at least one of the TCE rinses (refer to Section 4.2 for rinsing techniques). Cap or seal the open ends of the probe liners and nozzles to prevent contamination during shipping.

Prepare silica gel portions and glass filters as specified in Method 5, Section 4.1.1.

4.1.2 Preliminary Determinations. Select the sampling site, probe nozzle, and probe length as specified in Method 5, Section 4.1.2.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures section of the applicable regulation. Follow the guidelines outlined in Method 5, Section 4.1.2.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures section of the applicable regulation. Follow the guidelines outlined in Method 5, Section 4.1.2, for sampling time per point and total sample volume collected.

4.1.3 Preparation of Collection Train. Prepare the collection train as specified in Method 5, Section 4.1.3, with the addition of the following:

Set up the sampling train as shown in Figure 5-1 of Method 5 with the addition of the precollector cyclone, if used, between the probe and filter holder. The temperature of the precollector cyclone, if used, should be about the same as for the filter, i.e., 42 deg. +/- 10 deg. C (108 deg. +/- 18 deg. F). Use no stopcock grease on ground glass joints unless the grease is insoluble in TCE.

4.1.4 Leak Check Procedures. Follow the procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak Check During Sample Run), and 4.1.4.3 (Post-Test Leak Check).

4.1.5 Particulate Train Operation. Operate the sampling train as described in Method 5, Section 4.1.5, except maintain the gas temperature exiting the filter at 42 deg. +/- 10 deg. C (108 deg. +/- 18 deg. F).

4.1.6 Calculation of Percent Isokinetic. Same as in Method 5, Section 4.1.6.

4.2 Sample Recovery. Using the procedures and techniques described in Method 5, Section 4.2, quantitatively recover any particulate matter into the following containers (additions and deviations to the stated procedures are as noted):

4.2.1 Container No. 1 (Filter). Same instructions as Method 5, Section 4.2, "Container No. 1." If it is necessary to fold the filter, do so such that the film of oil is inside the fold.

4.2.2 Container No. 2 (Probe to Filter Holder). Taking care to see that material 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, precollector cyclone and collector flask (if used), and front half of the filter holder by washing these components with TCE and placing the wash in a glass container. Carefully measure the total amount of TCE used in the rinses. Perform the TCE rinses as described in Method 5, Section 4.2, "Container No. 2," using TCE instead of acetone.

Brush and rinse the inside of the cyclone, cyclone collection flask, and the front half of the filter holder. Brush and rinse each surface three times or more, if necessary, to remove visible particulate.

4.2.3 Container No. 3 (Silica Gel). Same procedure as in Method 5, Section 4.2, "Container No. 3."

4.2.4 Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Follow the same procedure as in Method 5, Section 4.2, "Impinger Water."

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

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5A-1. Handle each sample container as follows:

4.3.1 Container No. 1 (Filter). Transfer the filter from the sample container to a tared glass weighing dish and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Rinse Container No. 1 with a measured amount of TCE and analyze this rinse with the contents of Container No. 2. Weigh the filter to a constant weight. For the purpose of Section 4.3, the term "constant weight" means a difference of no more than 10 percent or 2 mg (whichever is greater) between two consecutive weighings made 24 hours apart. Report the "final weight" to the nearest 0.1 mg as the average of these two values.

4.3.2 Container No. 2 (Probe to Filter Holder). Before adding the rinse from Container No. 1 to 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 noticeable leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to correct the final results.

Measure the liquid in this container either volumetrically to  $\pm 1$  ml or gravimetrically to  $\pm 0.5$  g. Check to see if there is any appreciable quantity of condensed water present in the TCE rinse (look for a boundary layer or phase separation). If the volume of condensed water appears larger than 5 ml, separate the oil-TCE fraction from the water fraction using a separatory funnel. Measure the volume of the water phase to the nearest ml; adjust the stack gas moisture content, if necessary (see Sections 6.4 and 6.5). Next, extract the water phase with several 25-ml portions of TCE until, by visual observation, the TCE does not remove any additional organic material. Evaporate the remaining water fraction to dryness at 93 deg. C (200 deg. F), desiccate for 24 hours, and weigh to the nearest 0.1 mg.

Treat the total TCE fraction (including TCE from the filter container rinse and water phase extractions) as follows: Transfer the TCE and oil to a tared beaker and evaporate at ambient temperature and pressure. The evaporation of TCE from the solution may take several days. Do not desiccate the sample until the solution reaches an apparent constant volume or until the odor of TCE is not detected. When it appears that the TCE has evaporated, desiccate the sample and weigh it at 24-hour intervals to obtain a "constant weight" (as defined for Container No. 1 above). The "total weight" for Container No. 2 is the sum of the evaporated particulate weight of the TCE-oil and water phase fractions. Report the results to the nearest 0.1 mg.

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

4.3.4 "TCE Blank" Container. Measure TCE in this container either volumetrically or gravimetrically. Transfer

the TCE 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: In order to facilitate the evaporation of TCE liquid samples, these samples may be dried in a controlled temperature oven at temperatures up to 38 deg. C (100 deg. F) until the liquid is evaporated.

4.4 Quality Control Procedures. A quality control (QC) check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure defined in Method 5, Section 4.4.

### 5. Calibration

Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (5.1), Pitot Tube Assembly (5.2), Metering System (5.3), Probe Heater (5.4), Temperature Gauges (5.5), Leak Check of Metering System (5.6), and Barometer (5.7).

### 6. Calculations

6.1 Nomenclature. Same as in Method 5, Section 6.1, with the following additions:

$C[t]$  = TCE blank residue concentration, mg/mg.

$m[t]$  = Mass of residue of TCE after evaporation, mg.

$V[pc]$  = Volume of water collected in precollector, ml.

$V[t]$  = Volume of TCE blank, ml.

$V[tw]$  = Volume of TCE used in wash, ml.

$W[t]$  = Weight of residue in TCE wash, mg.  $\rho[t]$  = Density of TCE, mg/ml (see label on bottle).

6.2 Dry Gas Meter Temperature and Orifice Pressure Drop. Using the data obtained in this test, calculate the average dry gas meter temperature and average orifice pressure drop (see Figure 5-2 of Method 5).

6.3 Dry Gas Volume. Using the data from this test, calculate  $V[m(std)]$  by using Equation 5-1 of Method 5. If necessary, adjust the volume for leakages.

6.4 Volume of Water Vapor.

$$V[w(std)] = K[l] (V[lc] + V[pc])$$

Eq. 5A-1

Where:

$K[l] = 0.00133 \text{ m}^3/\text{ml}$  for metric units.

$= 0.04707 \text{ ft}^3/\text{ml}$  for English units.

6.5 Moisture Content.

$$B[ws] = V[w(std)] / [V[m(std)] + V[w(std)]]$$

Eq. 5A-2

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 and precollector analysis (Equations 5A-1 and 5A-2) and a second from the assumption of saturated conditions. The lower of the two values of moisture content 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 purpose of this method, the average stack gas temperature from Figure 5-2 of Method 5 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is within +/- 1 deg. C (2 deg. F).

6.6 TCE Blank Concentration.

$$C[t] = m[t] / V[t \text{ rho } t]$$

Eq. 5A-3

6.7 TCE Wash Blank.

$$W[t] = C[t]V[tw \text{ rho } t]$$

Eq. 5A-4

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from Containers 1, 2, and 3, less the TCE blank.

6.9 Particulate Concentration.

$$c[s] = K[2]m[n] / V [m(\text{std})]$$

Eq. 5A-5

Where:

$$K[2] = 0.001 \text{ g/mg.}$$

6.10 Isokinetic Variation and Acceptable Results. Same as in Method 5, Sections 6.11 and 6.12, respectively.

## 7. Bibliography

The bibliography for Method 5A is the same as that for Method 5.

## METHOD 5B -- DETERMINATION OF NONSULFURIC ACID PARTICULATE MATTER FROM STATIONARY SOURCES

### 1. Applicability and Principle.

1.1 Applicability. This method is to be used for determining nonsulfuric acid particulate matter from stationary sources. Use of this method must be specified by an applicable subpart, or approved by the Administrator, U.S. Environmental Protection Agency, for a particular application.

1.2 Principle. Particulate matter is withdrawn isokinetically from the source using the Method 5 train at 160

deg. C (320 deg. F). The collected sample is then heated in the oven at 160 deg. C (320 deg. F) for 6 hours to volatilize any condensed sulfuric acid that may have been collected, and the nonsulfuric acid particulate mass is determined gravimetrically.

## 2. Procedure.

The procedure is identical to EPA Method 5 except for the following:

2.1 Initial Filter Tare. Oven dry the filter at 160 +/- 5 deg. C (320 +/- 10 deg. F) for 2 to 3 hours, cool in a desiccator for 2 hours, and weigh. Desiccate to constant weight to obtain the initial tare. Use the applicable specifications and techniques of Section 4.1.1 of Method 5 for this determination.

2.2 Probe and Filter Temperatures. Maintain the probe outlet and filter temperatures at 160 +/- 14 deg. C (320 +/- 25 deg. F).

2.3 Analysis. Dry the probe sample at ambient temperature. Then oven-dry the probe and filter samples at a temperature of 160 +/- 5 deg. C (320 +/- 10 deg. F) for 6 hours. Cool in a desiccator for 2 hours, and weigh to constant weight. Use the applicable specifications and techniques of Section 4.3 of Method 5 for this determination.

METHOD 5C -- [RESERVED]

## METHOD 5D -- DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM POSITIVE PRESSURE FABRIC FILTERS

### 1. Applicability and Principle

1.1 Applicability. This method applies to the determination of particulate matter emissions from positive pressure fabric filters. Emissions are determined in terms of concentration (mg/m<sup>3</sup>) and emission rate (kg/h).

The General Provisions of 40 CFR Part 60, § 60.8(e), require that the owner or operator of an affected facility shall provide performance testing facilities. Such performance testing facilities include sampling ports, safe sampling platforms, safe access to sampling sites, and utilities for testing. It is intended that affected facilities also provide sampling locations that meet the specification for adequate stack length and minimal flow disturbances as described in Method 1. Provisions for testing are often overlooked factors in designing fabric filters or are extremely costly. The purpose of this procedure is to identify appropriate alternative locations and procedures for sampling the emissions from positive pressure fabric filters. The requirements that the affected facility owner or operator provide adequate access to performance testing facilities remain in effect.

1.2 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature at or above the exhaust gas temperature up to a nominal 120 deg. C (120 +/- 14 deg. C or 248 +/- 25 deg. F). The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

### 2. Apparatus

The equipment requirements for the sampling train, sample recovery, and analysis are the same as specified in Sections 2.1, 2.2, and 2.3, respectively, of Method 5 or Method 17.

### 3. Reagents

The reagents used in sampling, sample recovery, and analysis are the same as specified in Sections 3.1, 3.2, and

3.3, respectively, of Method 5 or Method 17.

#### 4. Procedure

4.1 Determination of Measurement Site. The configurations of positive pressure fabric filter structures frequently are not amenable to emission testing according to the requirements of Method 1. Following are several alternatives for determining measurement sites for positive pressure fabric filters.

4.1.1 Stacks Meeting Method 1 Criteria. Use a measurement site as specified in Method 1, Section 2.1.

4.1.2 Short Stacks Not Meeting Method 1 Criteria. Use stack extensions and the procedures in Method 1. Alternatively, use flow straightening vanes of the "egg-crate" type (see Figure 5D-1). Locate the measurement site downstream of the straightening vanes at a distance equal to or greater than two times the average equivalent diameter of the vane openings and at least one-half of the overall stack diameter upstream of the stack outlet.

4.1.3 Roof Monitor or Monovent. (See Figure 5D-2.) For a positive pressure fabric filter equipped with a peaked roof monitor, ridge vent, or other type of monovalent, use a measurement site at the base of the monovalent. Examples of such locations are shown in Figure 5D-2. The measurement site must be upstream of any exhaust point (e.g., louvered vent).

4.1.4 Compartment Housing. Sample immediately downstream of the filter bags directly above the tops of the bags as shown in the examples in Figure 5D-2. Depending on the housing design, use sampling ports in the housing walls or locate the sampling equipment within the compartment housing.

4.2 Determination of Number and Location of Traverse Points. Locate the traverse points according to Method 1, Section 2.3. Because a performance test consists of at least three test runs and because the varied configurations of positive pressure fabric filters, there are several schemes by which the number of traverse points can be determined and the three test runs can be conducted.

4.2.1 Single Stacks Meeting Method 1 Criteria. Select the number of traverse points according to Method 1. Sample all traverse points for each test run.

4.2.2 Other Single Measurement Sites. For a roof monitor or monovalent, single compartment housing, or other stack not meeting Method 1 criteria, use at least 24 traverse points. For example, for a rectangular measurement site, such as a monovalent, use a balanced 5 x 5 traverse point matrix. Sample all traverse points for each test run.

4.2.3 Multiple Measurement Sites. Sampling from two or more stacks or measurement sites may be combined for a test run, provided the following guidelines are met:

(a) All measurement sites up to 12 must be sampled. For more than 12 measurement sites, conduct sampling on at least 12 sites or 50 percent of the sites, whichever is greater. The measurement sites sampled should be evenly, or nearly evenly, distributed among the available sites; if not, all sites are to be sampled.

(b) The same number of measurement sites must be sampled for each test run.

(c) The minimum number of traverse points per test run is 24. An exception to the 24-point minimum would be a test combining the sampling from two stacks meeting Method 1 criteria for acceptable stack length, and Method 1 specifies fewer than 12 points per site.

(d) As long as the 24 traverse points per test run criterion is met, the number of traverse points per measurement site may be reduced to eight.

Alternatively, conduct a test run for each measurement site individually using the criteria in Section 4.2.1 or 4.2.2 for number of traverse points. Each test run shall count toward the total of three required for a performance test. If more than three measurement sites are sampled, the number of traverse points per measurement site may be reduced to eight as long as at least 72 traverse points are sampled for all the tests.

The following examples demonstrate the procedures for sampling multiple measurement sites.

Example 1: A source with nine circular measurement sites of equal areas may be tested as follows: For each test run, traverse three measurement sites using four points per diameter (eight points per measurement site). In this manner, test run number 1 will include sampling from sites 1, 2, and 3; run 2 will include samples from sites 4, 5, and 6; and run 3 will include sites 7, 8, and 9. Each test area may consist of a separate test of each measurement site using eight points. Use the results from all nine tests in determining the emission average.

Example 2: A source with 30 rectangular measurement sites of equal areas may be tested as follows: For each of three test runs, traverse five measurement sites using a 3 x 3 matrix of traverse points for each site. In order to distribute the sampling evenly over all the available measurement sites while sampling only 50 percent of the sites, number the sites consecutively from 1 to 30 and sample all the even numbered (or odd numbered) sites. Alternatively, conduct a separate test of each of 15 measurement sites using Section 4.2.1 or 4.2.2 to determine the number and location of traverse points, as appropriate.

Example 3: A source with two measurement sites of equal areas may be tested as follows: For each test of three test runs, traverse both measurement sites using Section 4.2.3 in determining number of traverse points. Alternatively, conduct two full emission test runs of each measurement site using the criteria in Section 4.2.1 or 4.2.2 to determine the number of traverse points.

Other test schemes, such as random determination of traverse points for a large number of measurement sites, may be used with prior approval from the Administrator.

4.3 Velocity Determination. The velocities of exhaust gases from positive pressure baghouses are often too low to measure accurately with the type S pilot specified in Method 2 [i.e., velocity head < 1.3 mm H<sub>2</sub>O (0.05 in. H<sub>2</sub>O)]. For these conditions, measure the gas flow rate at the fabric filter inlet following the procedures in Method 2.

Calculate the average gas velocity at the measurement site as follows:

$$v = Q[i] / A[o] * T[o] / T[i]$$

Eq. 5D-1

Where:

v = Average gas velocity at the measurement site(s), m/s (ft/s).

Q[i] = Inlet gas volume flow rate, m<sup>3</sup>/s (ft<sup>3</sup>/s).

A[o] = Measurement site(s) total cross-sectional area, m<sup>2</sup> (ft<sup>2</sup>).

T[o] = Temperature of gas at measurement site, deg. K (deg. R).

T[i] = Temperature of gas at inlet, deg. K (deg. R).

Use the average velocity calculated for the measurement site in determining and maintaining isokinetic sampling rates. Note: All sources of gas leakage, into or out of the fabric filter housing between the inlet measurement site and the outlet measurement site must be blocked and made leak-tight.

Velocity determinations at measurement sites with gas velocities within the range measurable with the type S pitot [i.e., velocity head > 1.3 mm H<sub>2</sub>O (0.05 in. H<sub>2</sub>O)] shall be conducted according to the procedures in Method 2.

4.4 Sampling. Follow the procedures specified in Section 4.1 of Method 5 or Method 17 with the exceptions as noted above.

4.5 Sample Recovery. Follow the procedures specified in Section 4.2 of Method 5 or Method 17.

4.6 Sample Analysis. Follow the procedures specified in Section 4.3 of Method 5 or Method 17.

4.7 Quality Control Procedures. A QC check of the volume metering system at the field site is suggested before collecting the sample. Use the procedure defined in Section 4.4 of Method 5.

## 5. Calibration

Follow the procedures as specified in Section 5 of Method 5 or Method 17.

## 6. Calculations

Follow the procedures as specified in Section 6 of Method 5 or Method 17 with the exceptions as follows:

6.1 Total volume flow rate may be determined using inlet velocity measurements and stack dimensions.

6.2 Average Particulate Concentration. For multiple measurement sites, calculate the average particulate concentration as follows:

$$C = \frac{\sum_{i=1}^n m[i]}{\sum_{i=1}^n \text{Vol}[i]}$$

Eq. 5D-2

Where:

$m[i]$  = The mass collected for run  $i$  of  $n$ , mg(gr).

$\text{Vol}[i]$  = The sample volume collected for run  $i$  of  $n$ ,  $\text{sm}^3$  (scf).

$C$  = Average concentration of particulate for all  $n$  runs, mg/ $\text{sm}^3$  (gr/scf).

## 7. Bibliography

The bibliography is the same as for Method 5.

Figure 5D-1. Example of flow straightening vanes.

[SEE FIGURE IN ORIGINAL]

Figure 5D-2. Acceptable sampling site locations for: (a) peaked roof; and (b) ridge vent type fabric filters.

[See figure in original]

## METHOD 5E--DETERMINATION OF PARTICULATE EMISSIONS FROM THE WOOL FIBERGLASS INSULATION MANUFACTURING INDUSTRY

### 1. *Applicability and Principle*

1.1 Applicability. This method is applicable for the determination of particulate emissions from wool fiberglass insulation manufacturing sources.

1.2 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 deg. +/- 14 deg. C (248 deg. +/- 25 deg. F) and in solutions of 0.1 N NaOH. The filtered particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water. The condensed particulate material collected in the impinger solutions is determined as total organic carbon (TOC) using a nondispersive infrared type of analyzer. The sum of the filtered particulate mass and the condensed particulate matter is reported as the total particulate mass.

### 2. *Apparatus*

2.1 Sampling Train. The equipment list for the sampling train is the same as described in Section 2.1 of Method 5 except as follows:

2.1.1 Probe Liner. Same as described in Section 2.1.2 of Method 5 except use only borosilicate or quartz glass liners.

2.1.2 Filter Holder. Same as described in Section 2.1.5 of the Method 5 with the addition of a leak-tight connection in the rear half of the filter holder designed for insertion of a thermocouple or other temperature gauge for measuring the sample gas exist temperature.

2.2 Sample Recovery. The equipment list for sample recovery is the same as described in Section 2.2 of Method 5 except three wash bottles are needed instead of two and only glass storage bottles and funnels may be used.

2.3 Analysis. The equipment list for analysis is the same as Section 2.3 of Method 5 with the additional equipment for TOC analysis as described below:

2.3.1 Sample Blender or Homogenizer. Waring type of ultrasonic.

2.3.2 Magnetic Stirrer.

2.3.3 Hypodermic Syringe. 0- to 100-  $\mu$ l capacity.

2.3.4 Total Organic Carbon Analyzer. Beckman Model 915 with 215 B infrared analyzer or equivalent and a recorder.

2.3.5 Beaker. 30 ml.

2.3.6 Water Bath. Temperature-controlled.

2.3.7 Volumetric Flasks. 1,000 ml and 500 ml.

### 3. Reagents

3.1 Sampling. The reagents used in sampling are the same as used in Reference Method 5 with the addition of 0.1 N NaOH (dissolve 40 g of ACS reagent grade NaOH in distilled water and dilute to 1 liter).

3.2 Sample Recovery. The reagents used in sample recovery are the same as used in Method 5 with the addition of distilled water and 0.1 N NaOH as described in Section 3.1.

3.3 Analysis. The reagents used in analysis are the same as in Method 5 except as follows:

3.3.1 Carbon Dioxide-Free Water. Distilled or deionized water that has been freshly boiled for 15 minutes and cooled to room temperature while preventing exposure to ambient air with a cover vented with an ascarite tube.

3.3.2 Hydrochloric Acid. HCl, concentrated, with a dropper.

3.3.3 Organic Carbon Stock Solution. Dissolve 2.1254 g of dried potassium biphthalate in CO<sub>2</sub>-free water and dilute to 1 liter in a volumetric flask. This solution contains 1,000 mg/l organic carbon.

3.3.4 Inorganic Carbon Stock Solution. Dissolve 4.404 g anhydrous sodium carbonate in about 500 ml of CO<sub>2</sub>-free water in a 1 liter volumetric flask. Add 3.497 g anhydrous sodium bicarbonate to the flask and dilute to 1 liter with CO<sub>2</sub>-free water. This solution contains 1,000 mg/l inorganic carbon.

3.3.5 Oxygen Gas. CO<sub>2</sub>-free.

### 4. Procedure

4.1 Sampling. The sampling procedures are the same as in Section 4.1 of Method 5 except as follows:

4.1.1 Filtration Temperature. The temperature of the filtered gas stream, rather than the filter compartment air temperature, is maintained at 120 deg. +/- 14 deg. C (248 deg. +/- 25 deg. F).

4.1.2 Impinger Solutions. 0.1 N NaOH is used in place of water in the impingers. The volumes of the solutions are the same as in Method 5.

4.2 Sample Recovery. The sample recovery procedure is as follows:

Water is used to rinse and clean the probe parts prior to the acetone rinse. Save portions of the water, acetone, and 0.1 N NaOH used for cleanup as blanks following the procedure as in Section 4.2 of Method 5.

NOTE: All parts of the sample collection portion of the train (e.g., probe and nozzle, filter holder, impinger glassware) must be free of organic solvent residue before sample collection. It is necessary that all sampling apparatus that have been rinsed with acetone be flushed twice with water or dilute NaOH before the sample run. The rinse solutions from this cleaning process should be discarded. If other solvents that are not readily soluble in water (e.g., TCE) are used, place the exposed sampling apparatus in a drying oven at 105 deg. C for at least 30 minutes.

*Container No. 1.* The filter is removed and stored in the same manner as in Section 4.2 of Method 5.

*Container No. 2.* Use water to rinse the sample nozzle, probe, and front half of the filter holder three times in the manner described in Section 4.2 of Method 5 except that no brushing is done. Put all the wash water in one container, seal, and label.

*Container No. 3.* Rinse and brush the sample nozzle, probe, and front half of the filter holder with acetone as described for Container No. 2. in Section 4.2 of Method 5.

*Container No. 4.* Place the contents of the silica gel impinger in its original container as described for Container No. 3 in Section 4.2 of Method 5.

*Container No. 5.* Measure the liquid in the first three impingers and record the volume or weight as described for the Impinger Water in Section 4.2 of Method 5. Do not discard this liquid, but place it in a sample container using a glass funnel to aid in the transfer from the impingers or graduated cylinder (if used) to the sample container. Rinse each impinger thoroughly with 0.1 N NaOH three times, as well as the graduated cylinder (if used) and the funnel, and put these rinsings in the same sample container. Seal the container and label to identify its contents clearly.

4.3 Analysis. The procedures for analysis are the same as in Section 4.3 of Method 5 with exceptions noted as follows:

*Container No. 1.* Determination of weight gain on the filter is the same as described for Container No. 1 in Section 4.3 of Method 5 except that the filters must be dried at 20 deg. +/- 6 deg. C (68 deg. F +/- 10 deg. F) and at ambient pressure.

*Containers Nos. 2 and 3.* Analyze the contents of Containers Nos. 2 and 3 as described for Container No. 2 in Section 4.3 of Method 5 except that evaporation of the samples must be at 20 deg. +/- 6 deg. C (68 deg. +/- 10 deg. F) and at ambient pressure.

*Container No. 4.* Weigh the spent silica gel as described for Container No. 3 in Section 4.3 of Method 5.

*"Water and Acetone Blank" Containers.* Determine the water and acetone blank values following the procedures for Acetone Blank Container in Section 4.3 of Method 5. Evaporate the samples at ambient temperature [20 deg. +/- 6 deg. C (68 deg. +/- 10 deg. F)] and pressure.

*Container No. 5.* For the determination of total organic carbon, perform two analyses on successive identical samples, i.e., total carbon and inorganic carbon. The desired quantity is the difference between the two values obtained. Both analyses are based on conversion of sample carbon into carbon dioxide for measurement by a nondispersive infrared analyzer. Results of analyses register as peaks on a strip chart recorder.

The principal differences between operating parameters for the two channels involve the combustion tube packing material and temperature. In the total carbon channel, a high temperature [950 deg. C (1740 deg. F)] furnace heats a Hastelloy combustion tube packed with cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier gas, the elevated temperature, and catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO<sub>2</sub> and steam. In the inorganic carbon channel, a low temperature [150 deg. C (300 deg. F)] furnace heats a glass tube containing quartz chips wetted with 85 percent phosphoric acid. The acid liberates CO<sub>2</sub> and steam from inorganic carbonates. The operating temperature is below that required to oxidize organic matter. Follow the manufacturer's instructions for assembly, testing, calibration, and operation of the analyzer.

As samples collected in 0.1 N NaOH often contain a high measure of inorganic carbon that inhibits repeatable determinations of TOC, sample pretreatment is necessary. Measure and record the liquid volume of each sample. If the sample contains solids or an immiscible liquid, homogenize the sample with a blender or ultrasonics until satisfactory repeatability is obtained. Transfer a representative portion of 10 to 15 ml to a 30-ml beaker, acidify with about 2 drops of concentrated HCl to a pH of 2 or less. Warm the acidified sample at 50 deg. C (120 deg. F) in a water bath for 15 minutes. While stirring the sample with a magnetic stirrer, withdraw a 20- to 50- $\mu$ l sample from the beaker and inject it into the total carbon port of the analyzer. Measure the peak

height. Repeat the injections until three consecutive peaks are obtained within +/- 10 percent of the average.

Repeat the analyses for all the samples and the 0.1 N NaOH blank. Prepare standard curves for total carbon and for inorganic carbon of 10, 20, 30, 40, 50, 60, 80, and 100 mg/l by diluting with CO<sub>2</sub>-free water 10, 20, 30, 40, and 50 ml of the two stock solutions to 1,000 ml and 30, 40, and 50 ml of the two stock solutions to 500 ml. Inject samples of these solutions into the analyzer and record the peak heights as described above. The acidification and warming steps are not necessary for preparation of the standard curve.

Ascertain the sample concentrations for the samples from the corrected peak heights for the samples by reference to the appropriate standard curve. Calculate the corrected peak height for the standards and the samples by deducting the blank correction as follows:

$$\text{Corrected peak height} = A - B$$

Eq. 5E-1

Where:

A = Peak height of standard or sample, mm or other appropriate unit.

B = Peak height of blank, mm or other appropriate unit.

If samples must be diluted for analysis, apply an appropriate dilution factor.

### 5. Calibration

Calibration of sampling and analysis equipment is the same as in Section 5 of Method 5 with the addition of the calibration of the TOC analyzer described in Section 4.3 of this method.

### 6. Calculations

The calculations and nomenclature for the calculations are the same as described in Section 6 of Method 5 with the addition of the following:

#### 6.1 Mass of Condensed Particulate Material Collected.

$$m[c] = 0.001 C[\text{toc}] V[s]$$

Eq. 5E-2

Where:

0.001 = Liters per milliliter.

m[c] = Mass of condensed particulate material collected in the impingers measured as TOC, mg.

C[toc] = Concentration of TOC in the liquid sample from TOC analysis in Section 4.3, mg/l.

V[s] = Total volume of liquid sample, ml.

#### 6.2 Concentration of Condensed Particulate Material.

$$C[c] = 0.001 [m[c] / V[m(std)]]$$

Eq. 5E-3

Where:

0.001 = Grams per milligram.

$C[c]$  = Concentration of condensed particulate matter in stack gas, dry basis, corrected to standard condition, g/dscm.

$V[m(std)]$  = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm, from Section 6.3 of Method 5.

6.3 Total Particulate Concentration.

$$C[t] = C[s] + C[c]$$

Eq. 5E-4

Where:

$C[t]$  = Total particulate concentration, dry basis, corrected to standard conditions, g/dscm.

$C[s]$  = Concentration of filtered particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm, from Equation 5-6 of Method 5.

## 7. Bibliography

The bibliography is the same as in Method 5 with the addition of the following:

1. American Public Health Association, American Water Works Association, Water Pollution Control Federation. Standard Methods for the Examination of Water and Wastewater. Fifteenth Edition. Washington, DC 1980.

## METHOD 5F--DETERMINATION OF NONSULFATE PARTICULATE MATTER FROM STATIONARY SOURCES

### 1. *Applicability and Principle.*

1.1 Applicability. This method is to be used for determining nonsulfate particulate matter from stationary sources. Use of this method must be specified by an applicable subpart of the standards, or approved by the Administrator, U.S. Environmental Protection Agency, for a particular application.

1.2 Principle. Particulate matter is withdrawn isokinetically from the source using the Method 5 train at 160 deg. C (320 deg. F). The collected sample is then extracted with water. A portion of the extract is analyzed for sulfate content. The remainder is neutralized with ammonium hydroxide before it is dried and weighed.

### 2. *Apparatus.*

The apparatus is the same as Method 5 with the following additions.

## 2.1 Analysis.

2.1.1 Erlenmeyer Flasks. 125-ml, with ground glass joints.

2.1.2 Air Condenser. With ground glass joint compatible with the Erlenmeyer flasks.

2.1.3 Beakers. 250-ml.

2.1.4 Volumetric Flasks. 1-liter, 500-ml (one for each sample), 200-ml, and 50-ml (one for each sample and standard).

2.1.5 Pipets. 5-ml (one for each sample and standard).

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

2.1.6.1 Columns. An anion separation or other column capable of resolving the sulfate ion from other species present and a standard anion suppressor column. 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. Other systems which do not use suppressor columns may also be used.

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

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

2.1.6.4 Conductivity Detector.

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

## 3. Reagents.

The reagents are the same as for Method 5 with the following exceptions:

3.1 Sample Recovery. Water, deionized distilled to conform to American Society for Testing and Materials Specification D1193-74, Type 3, is needed. At the option of the analyst, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.2 Analysis. The following are required:

3.2.1 Water. Same as in Section 3.1.

3.2.2 Stock Standard Solution, 1 mg  $(\text{NH}_4)_2\text{SO}_4$ /ml. Dry an adequate amount of primary standard grade ammonium sulfate at 105 deg. to 110 deg. C for a minimum of 2 hours before preparing the standard solution. Then dissolve exactly 1,000 g of dried  $(\text{NH}_4)_2\text{SO}_4$  in water in a 1-liter volumetric flask, and dilute to 1 liter. Mix well.

3.2.3 Working Standard Solution, 25  $\mu\text{g}$   $(\text{NH}_4)_2\text{SO}_4$ /ml. Pipet 5 ml of the stock standard solution into a 200-ml volumetric flask. Dilute to 200 ml with water.

3.2.4 Eluent Solution. Weight 1.018 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 1.008 g of sodium bicarbonate ( $\text{NaHCO}_3$ ), and dissolve in 4 liters of water. This solution is 0.0024 M  $\text{Na}_2\text{CO}_3$ /0.003 M  $\text{NaHCO}_3$ . Other eluents appropriate to the column type and capable of resolving sulfate ion from other species present may be used.

3.2.5 Ammonium Hydroxide. Concentrated, 14.8 M.

3.2.6 Phenolphthalein Indicator. 3,3-Bis(4-hydroxyphenyl)-1-(3H)-isobenzofuranone. Dissolve 0.05 g in 50 ml of ethanol and 50 ml of water.

#### 4. Procedure.

4.1 Sampling. The sampling procedure is the same as Method 5, Section 4.1, except that the probe outlet and filter temperatures shall be maintained at 160 deg. +/- 14 deg. C (320 deg. +/- 25 deg. F).

4.2 Sample Recovery. The sample recovery procedure is the same as Method 5, Section 4.2, except that the recovery solvent shall be water instead of acetone.

#### 4.3 Analysis.

4.3.1 Sample Extraction. Cut the filter into small pieces, and place it in a 125-ml Erlenmeyer flask with a ground glass joint equipped with an air condenser. Rinse the shipping container with water, and pour the rinse into the flask. Add additional water to the flask until it contains about 75 ml, and place the flask on a hot plate. Gently reflux the contents for 6 to 8 hours. Cool the solution, and transfer it to a 500-ml volumetric flask. Rinse the Erlenmeyer flask with water, and transfer the rinsings to the volumetric flask including the pieces of filter.

Transfer the probe rinse to the same 500-ml volumetric flask with the filter sample. Rinse the sample bottle with water, and add the rinsings to the volumetric flask. Dilute the sample to exactly 500 ml with water.

4.3.2 Sulfate (SO<sub>4</sub>) Analysis. Allow the sample to settle until all solid material is at the bottom of the volumetric flask. If necessary, centrifuge a portion of the sample. Pipet 5 ml of the sample into a 50-ml volumetric flask, and dilute to 50 ml with water. Prepare a standard calibration curve according to Section 5.1. 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 analysis 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, sulfate retention time, flow rate, detector sensitivity setting, and recorder chart speed.

4.3.3 Sample Residue. Transfer the remaining contents of the volumetric flask to a tared 250-ml beaker. Rinse the volumetric flask, and add the rinsings to the tared beaker. Make certain that all particulate matter is transferred to the beaker. Evaporate the water in an oven heated to 105 deg. C until only about 100 ml of water remains. Remove the beakers from the oven, and allow them to cool.

After the beakers have cooled, add five drops of phenolphthalein indicator, and then add concentrated ammonium hydroxide until the solution turns pink. Return the samples to the oven at 105 deg. C, and evaporate the samples to dryness. Cool the samples in a desiccator, and weigh the samples to constant weight.

#### 4.4 Blanks.

4.4.1 Filter Blank. Choose a clean filter from the same lot as those used in the testing. Treat the blank filter as a sample, and analyze according to Sections 4.3.1 and 4.3.2.

4.4.2 Water. Transfer a measured volume of water between 100 and 200 ml into a tared 250-ml beaker. Treat

the blank as a sample, and analyze according to Section 4.3.3.

## 5. Calibration.

The calibration procedure is the same as Method 5, Section 5, with the following additions:

5.1 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  $\mu$ g/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250  $\mu$ g.) Dilute each flask to volume with water, and mix well. Analyze with the samples as described in Section 4.3. Prepare or calculate a linear regression plot of the standard masses in  $\mu$ g (x-axis) versus their responses (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this line, or equation, determine the slope, and calculate its reciprocal which is 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 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  $\mu$ g).

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

## 6. Calculations.

Calculations are the same as Method 5, Section 6, with the following additions:

### 6.1 Nomenclature.

C[w] = Water blank residue concentration, mg/ml.

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

H[s] = Sample response, mm for height or  $\text{mm}^2$  for area.

H[b] = Filter blank response, mm for height or  $\text{mm}^2$  for area.

m[b] = Mass of beaker used to dry sample, mg.

m[f] = Mass of sample filter, mg.

m[n] = Mass of nonsulfate particulate matter, mg.

m[s] = Mass of ammonium sulfate in the sample, mg.

m[t] = Mass of beaker, filter, and dried sample, mg.

m[w] = Mass of residue after evaporation of water blank, mg.

S = Calibration factor,  $\mu$ g/mm.

V[b] = Volume of water blank, ml.

V[s] = Volume of sample evaporated, 495 ml.

## 6.2 Water Blank Concentration.

$$C[w] = m[w] / V[b]$$

Eq. 5F-1

## 6.3 Mass of Ammonium Sulfate.

$$m[s] = (99(H[s] - H[b])) / (1000)$$

Eq. 5F-2

## 6.4 Mass of Nonsulfate Particulate Matter.

$$m[n] = m[t] - m[b] - m[s] - m[f] - V[s]C[w]$$

Eq. 5F-3

## 7. *Alternative Procedures*

7.1 The following procedure may be used as an alternative to the procedure in Section 4.3.

7.1.1 Apparatus. Same as for Method 6, Sections 2.3.3 to 2.3.6 with the following additions.

7.1.1.1 Beakers. 250-ml, one for each sample, and 600-ml.

7.1.1.2 Oven. Capable of maintaining temperatures of 75 +/- 5 deg. C and 105 +/- 5 deg. C.

7.1.1.3 Buchner Funnel.

7.1.1.4 Glass Columns. 25-mm X 305-mm (1-in. X 12-in.) with Teflon stopcock.

7.1.1.5 Volumetric Flasks. 50-ml and 500-ml, one set for each sample, and 100-ml, 200-ml, and 1000-ml.

7.1.1.6 Pipettes. Two 20-ml and one 200-ml, one set for each sample, and 5-ml.

7.1.1.7 Filter Flasks. 500-ml

7.1.1.8 Polyethylene Bottle. 500-ml, one for each sample.

7.1.2 Reagents. Same as Method 6, Sections 3.3.2 to 3.3.5 with the following additions:

7.1.2.1 Water, Ammonium Hydroxide, and Phenolphthalein. Same as Sections 3.2.1, 3.2.5, and 3.2.6 of this method, respectively.

7.1.2.2 Filter. Glass fiber to fit Buchner funnel.

7.1.2.3 Hydrochloric Acid (HCl), 1 M. Add 8.3 ml of concentrated HCl (12 M) to 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.1.2.4 Glass Wool.

7.1.2.5 Ion Exchange Resin. Strong cation exchange resin, hydrogen form, analytical grade.

7.1.2.6 pH Paper. Range of 1 to 7.

7.1.3 Analysis.

7.1.3.1 Ion Exchange Column Preparation. Slurry the resin with 1 M HCl in a 250-ml beaker, and allow to stand overnight. Place 2.5 cm (1 in.) of glass wool in the bottom of the glass column. Rinse the slurried resin twice with water. Resuspend the resin in water, and pour sufficient resin into the column to make a bed 5.1 cm (2 in.) deep. Do not allow air bubbles to become entrapped in the resin or glass wool to avoid channeling, which may produce erratic results. If necessary, stir the resin with a glass rod to remove air bubbles. After the column has been prepared, never let the liquid level fall below the top of the upper glass wool plug. Place a 2.5-cm (1-in.) plug of glass wool on top of the resin. Rinse the column with water until the eluate gives a pH of 5 or greater as measured with pH paper.

7.1.3.2 Sample Extraction. Follow the procedure given in Section 4.3.1 except do not dilute the sample to 500 ml.

7.1.3.3 Sample Residue. Place at least one clean glass fiber filter for each sample in a Buchner funnel, and rinse the filters with water. Remove the filters from the funnel, and dry them in an oven at 105 +/- 5 deg. C; then cool in a desiccator. Weigh each filter to constant weight according to the procedure in Method 5, Section 4.3. Record the weight of each filter to the nearest 0.1 mg.

Assemble the vacuum filter apparatus, and place one of the clean, tared glass fiber filters in the Buchner funnel. Decant the liquid portion of the extracted sample (Section 7.1.3.2) through the tared glass fiber filter into a clean, dry, 500-ml filter flask. Rinse all the particulate matter remaining in the volumetric flask onto the glass fiber filter with water. Rinse the particulate matter with additional water. Transfer the filtrate to a 500-ml volumetric flask, and dilute to 500 ml with water. Dry the filter overnight at 105 +/- 5 deg. C, cool in a desiccator, and weigh to the nearest 0.1 mg.

Dry a 250-ml beaker at 75 +/- 5 deg. C, and cool in a desiccator; then weigh to constant weight to the nearest 0.1 mg. Pipette 200 ml of the filtrate that was saved into a tared 250-ml beaker; add five drops of phenolphthalein indicator and sufficient concentrated ammonium hydroxide to turn the solution pink. Carefully evaporate the contents of the beaker to dryness at 75 +/- 5 deg. C. Check for dryness every 30 minutes. Do not continue to bake the sample once it has dried. Cool the sample in a desiccator, and weigh to constant weight to the nearest 0.1 mg.

7.1.3.4 Sulfate Analysis. Adjust the flow rate through the ion exchange column to 3 ml/min. Pipette a 20-ml aliquot of the filtrate onto the top of the ion exchange column, and collect the eluate in a 50-ml volumetric flask. Rinse the column with two 15-ml portions of water. Stop collection of the eluate when the volume in the flask reaches 50-ml. Pipette a 20-ml aliquot of the eluate into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thiorin indicator, and titrate to a pink end point 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. Perform the ion exchange and titration procedures on duplicate portions of the filtrate. Results should agree within 5 percent. Regenerate or replace the ion exchange resin after 20 sample aliquotes have been analyzed or if the end point of the titration becomes unclear.

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

7.1.3.5 Blank Determination. Begin with a sample of water of the same volume as the samples being processed and carry it through the analysis steps described in Sections 7.1.3.3 and 7.1.3.4. A blank value larger than 5 mg

should not be subtracted from the final particulate matter mass. Causes for large blank values should be investigated and any problems resolved before proceeding with further analyses.

7.1.4 Calibration. Calibrate the barium perchlorate solutions as in Method 6, Section 5.5.

7.1.5 Calculations.

7.1.5.1 Nomenclature. Same as Section 6.1 with the following additions:

m[a] = Mass of clean analytical filter, mg.

m[d] = Mass of dissolved particulate matter, mg.

m[e] = Mass of beaker and dissolved particulate matter after evaporation of filtrate, mg.

m[p] = Mass of insoluble particulate matter, mg.

m[r] = Mass of analytical filter, sample filter, and insoluble particulate matter, mg.

m[bk] = Mass of nonsulfate particulate matter in blank sample, mg.

N = Normality of Ba(C10[4])[2] titrant, meq/ml.

V[a] = Volume of aliquot taken for titration, 20 ml.

V[c] = Volume of titrant used for titration blank, ml.

V[d] = Volume of filtrate evaporated, 200ml.

V[e] = Volume of eluate collected, 50 ml.

V[f] = Volume of extracted sample, 500 ml.

V[i] = Volume of filtrate added to ion exchange column, 20 ml.

V[t] = Volume of Ba(C10[4])[2] titrant, ml.

W = Equivalent weight of ammonium sulfate, 66.07 mg/meq.

7.1.5.2 Mass of Insoluble Particulate Matter.

$$m[p] = m[r] - m[a] - m[f]$$

Eq. 5F-4

7.1.5.3 Mass of Dissolved Particulate Matter.

$$m[d] = (m[e] - V[f] m[b]) / V[d]$$

Eq. 5F-5

7.1.5.4 Mass of Ammonium Sulfate.

$$m[s] = (V[t] - V[c]) N W V[e] V[f] / V[a] V[i]$$

Eq. 5F-6

7.1.5.5 Mass of Nonsulfate Particulate Matter.

$$m[n] = m[p] +/- m[d] - m[s] - m[bk]$$

Eq.5F-7

## 8. *Bibliography.*

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## METHOD 5G -- DETERMINATION OF PARTICULATE EMISSIONS FROM WOOD HEATERS FROM A DILUTION TUNNEL SAMPLING LOCATION

### 1. *Applicability and Principle*

1.1 Applicability. This method is applicable for the determination of particulate matter emissions from wood heaters.

1.2 Principle. Particulate matter is withdrawn proportionally at a single point from a total collection hood and sampling tunnel that combines the wood heater exhaust with ambient dilution air. The particulate matter is collected on two glass fiber filters in series. The filters are maintained at a temperature of no greater than 32 deg. C (90 deg. F). The particulate mass is determined gravimetrically after removal of uncombined water.

There are three sampling train approaches described in this method: (1) One dual-filter dry sampling train operated at about 0.015 m<sup>3</sup>/min, (2) One dual-filter plus impingers sampling train operated at about 0.015 m<sup>3</sup>/min, and (3) two dual-filter dry sampling trains operated simultaneously at any flow rate. Options (2) and (3) are referenced in Section 7 of this method. The dual-filter sampling train equipment and operation, option (1), are described in detail in this method.

### 2. *Apparatus*

2.1 Sampling Train. The sampling train configuration is shown in Figure 5G-1 and consists of the following components:

2.1.1 Probe. Stainless steel (e.g., 316 or grade more corrosion resistant) or glass about 95 mm (3/8 in.) I.D., 0.6 m (24 in.) in length. If made of stainless steel, the probe shall be constructed from seamless tubing.

2.1.2 Pitot Tube. Type S, as described in Section 2.1 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2, Section 4.

Alternatively, a standard pitot may be used as described in Method 2, Section 2.1.

2.1.3 Differential Pressure Gauge. Inclined manometer or equivalent device, as described in Method 2, Section 2.2. One manometer shall be used for velocity head ( $\Delta p$ ) readings and another (optional) for orifice differential pressure readings ( $\Delta H$ ).

2.1.4 Filter Holders. Two each made of borosilicate glass, stainless steel, or Teflon, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filters. The filter holders shall be placed in series with the backup filter holder located 25 to 100 mm (1 to 4 in.) downstream from the primary filter holder. The filter holder shall be capable of holding a filter with a 100 mm (4 in.) diameter, except as noted in Section 7.

NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

2.1.5 Filter Temperature Monitoring System. A temperature gauge capable of measuring temperature to within 1.5 percent of absolute temperature. The gauge shall be installed at the exit side of the front filter holder so that the sensing tip of the temperature gauge is in direct contact with the sample gas or in a thermowell as shown in Figure 5G-1. The temperature gauge shall comply with the calibration specifications in Method 2, Section 4. Alternatively, the sensing tip of the temperature gauge may be installed at the inlet side of the front filter holder.

2.1.6 Dryer. Any system capable of removing water from the sample gas to less than 1.5 percent moisture (volume percent) prior to the metering system. System includes monitor for demonstrating that sample gas temperature is less than 20 deg. C (68 deg. F).

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

2.1.8 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

2.1.9 Dilution Tunnel Gas Temperature Measurement. A temperature gauge capable of measuring temperature to within 1.5 percent of absolute temperature.

2.2 Dilution Tunnel. The dilution tunnel apparatus is shown in Figure 5G-2 and consists of the following components:

2.2.1 Hood. Constructed of steel with a minimum diameter of 0.3 m (1 ft) on the large end and a standard 0.15 to 0.3 m (0.5 to 1 ft) coupling capable of connecting to standard 0.15 to 0.3 m (0.5 to 1 ft) stove pipe on the small end.

2.2.2 90 deg. Elbows. Steel 90 deg. elbows, 0.15 to 0.3 m (0.5 to 1 ft) in diameter for connecting mixing duct, straight duct and damper (optional) assembly. There shall be at least two 90 deg. elbows upstream of the sampling section (see Figure 5G-2).

2.2.3 Straight Duct. Steel, 0.15 to 0.3 m (0.5 to 1 ft) in diameter to provide the ducting for the dilution apparatus upstream of the sampling section. Steel duct, 0.15 m (0.5 ft) in diameter shall be used for the sampling section. In the sampling section, at least 1.2 m (4 ft) downstream of the elbow, shall be two holes (velocity traverse ports) at 90 deg. to each other of sufficient size to allow entry of the pitot for traverse measurements. At least 1.2 m (4 ft) downstream of the velocity traverse ports, shall be one hole (sampling port) of sufficient size to

allow entry of the sampling probe. Ducts of larger diameter may be used for the sampling section, provided the specifications for minimum gas velocity and the dilution rate range shown in Section 4 are maintained. The length of duct from the hood inlet to the sampling ports shall not exceed 9.1 m (30 ft).

2.2.4 Mixing Baffles. Steel semicircles (two) attached at 90 deg. to the duct axis on opposite sides of the duct midway between the two elbows upstream of sampling section. The space between the baffles shall be about 0.3 m (12 in.).

2.2.5 Blower. Squirrel cage or other fan capable of extracting gas from the dilution tunnel of sufficient flow to maintain the velocity and dilution rate specifications in Section 4 and exhausting the gas to the atmosphere.

2.3 Sample Recovery. Probe brushes, wash bottles, sample storage containers, petri dishes, and a funnel as described in Method 5, Section 2.2.1 through 2.2.4, and 2.2.8, respectively, are needed.

2.4 Analysis. Glass weighing dishes, desiccator, analytical balance, beakers (250 ml or smaller), hygrometer, and temperature gauge as described in Method 5, Sections 2.3.1 through 2.3.3 and 2.3.5 through 2.3.7, respectively, are needed.

### 3. Reagents

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

3.1.1 Filters. Glass fiber filters with a minimum diameter of 100 mm (4 in.), without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. Gelman A/E 61631 has been found acceptable for this purpose.

3.1.2 Stopcock Grease. Same as Method 5, Section 3.1.5.

3.2 Sample Recovery. Acetone-reagent grade, same as Method 5, Section 3.2.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. As in Section 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

### 4. Procedure

4.1 Dilution Tunnel. A schematic of a dilution tunnel is shown in Figure 5G-2. The dilution tunnel dimensions and other features are described in Section 2.2. Assemble the dilution tunnel sealing joints and seams to prevent air leakage. Clean the dilution tunnel with an appropriately sized, wire chimney brush before each certification test.

4.1.1 Draft Determination. Prepare the wood heater as in Method 28, Section 6.2.1. Locate the dilution tunnel hood centrally over the wood heater stack exhaust. Operate the dilution tunnel blower at the flow rate to be used during the test run. Measure the draft imposed on the wood heater by the dilution tunnel (i.e., the difference in draft measured with and without the dilution tunnel operating) as described in Method 28, Section 6.2.3. Adjust the distance between the top of the wood heater stack exhaust and the dilution tunnel hood so that the dilution tunnel induced draft is less than 1.25 Pa (0.005 in. H<sub>2</sub>O). Have no fire in the wood heater, close the wood heater doors, and open fully the air supply controls during this check and adjustment.

4.1.2 Smoke Capture. During the pretest ignition period described in Method 28, Section 6.3, operate the

dilution tunnel and visually monitor the wood heater stack exhaust. Operate the wood heater with the doors closed and determine that 100 percent of the exhaust gas is collected by the dilution tunnel hood. If less than 100 percent of the wood heater exhaust gas is collected, adjust the distance between the wood heater stack and the dilution tunnel hood until no visible exhaust gas is escaping. Stop the pretest ignition period, and repeat the draft determination procedure described in Section 4.1.1.

4.2 Velocity Measurements. During the pretest ignition period described in Method 28, Section 6.3, conduct a velocity traverse to identify the point of average velocity. This single point shall be used for measuring velocity during the test run.

4.2.1 Velocity Traverse. Measure the diameter of the duct at the velocity traverse port location through both ports. Calculate the duct area using the average of the two diameters. A pretest leak-check of pitot lines as in Method 2, Section 3.1, is recommended. Place the calibrated pitot tube at the centroid of the stack in either of the velocity traverse ports. Adjust the damper or similar device on the blower inlet until the velocity indicated by the pitot is approximately 220 m/min (715 fpm). Continue to read the DELTA p and temperature until the velocity has remained constant (less than 5 percent change) for 1 minute. Once a constant velocity is obtained at the centroid of the duct, perform a velocity traverse as outlined in Method 2, Section 3.3 using four points per traverse as outlined in Method 1. Measure the DELTA p and tunnel temperature at each traverse point and record the readings. Calculate the total gas flow rate using calculations contained in Method 2, Section 5. Verify that the flow rate is  $4 \pm 0.45 \text{ m}^3/\text{min}$  (140  $\pm$  14 scfm); if not, readjust the damper, and repeat the velocity traverse. The moisture may be assumed to be 4 percent (100 percent relative humidity at 85 deg. F). Direct moisture measurements such as outlined in EPA Method 4 are also permissible.

NOTE: If burn rates exceed 3 kg/hr (6.6 lb/hr), dilution tunnel duct flow rates greater than  $4 \text{ m}^3/\text{min}$  (140 scfm) and sampling section duct diameters larger than 150 mm (6 in.) are allowed. If larger ducts or flow rate are used, the sampling section velocity shall be at least 220 m/min (715 fpm). In order to ensure measurable particulate mass catch, it is recommended that the ratio of the average mass flow rate in the dilution tunnel to the average fuel burn rate be less than 150:1 if larger duct sizes or flow rates are used.

4.2.2 Testing Velocity Measurements. After obtaining velocity traverse results that meet the flow rate requirements, choose a point of average velocity and place the pitot and thermocouple at that location in the duct. Alternatively, locate the pitot and thermocouple at the duct centroid and calculate a velocity correction factor for the centroidal position. Mount the pitot to ensure no movement during the test run and seal the port holes to prevent any air leakage. Align the pitot to be parallel with the duct axis, at the measurement point. Check that this condition is maintained during the test run (about 30-minute intervals). Monitor the temperature and velocity during the pretest ignition period to ensure the proper flow rate is maintained. Make adjustments to the dilution tunnel flow rate as necessary.

#### 4.3 Sampling.

4.3.1 Pretest Preparation. It is suggested that sampling equipment be maintained and calibrated according to the procedure described in APTD-0576.

Check and desiccate filters as described in Method 5, Section 4.1.1.

4.3.2 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.

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

Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct.

Set up the train as in Figure 5G-1.

#### 4.3.3 Leak-Check Procedures.

4.3.3.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, conduct the leak-check as described in Method 5, Section 4.1.4.1. A vacuum 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

4.3.3.2 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each test run. The leak-check shall be done in accordance with the procedures described in Method 5, Section 4.1.4.1. A vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

4.3.4 Preliminary Determinations. Determine the pressure, temperature and the average velocity of the tunnel gases as in Section 4.2. Moisture content of diluted tunnel gasses is assumed to be 4 percent for making flow rate calculations; the moisture content may be measured directly as in Method 4.

4.3.5 Sampling Train Operation. Position the probe inlet at the stack centroid, and block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream. Be careful not to bump the probe into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

Begin sampling at the start of the test run as defined in Method 28, Section 6.4.1. During the test run, maintain a sample flow rate proportional to the dilution tunnel flow rate (within 10 percent of the initial proportionality ratio) and a filter holder temperature of no greater than 32 deg. C (90 deg. F). The initial sample flow rate shall be approximately 0.015 m<sup>3</sup>/min (0.5 cfm).

For each test run, record the data required on a data sheet such as the one shown in Figure 5G-3. 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 and when sampling is halted. Take other readings as indicated on Figure 5G-3 at least once each 10 minutes during the test run. Since the manometer level and zero may drift because of vibrations and temperature changes, make periodic checks during the test run.

For the purposes of proportional sampling rate determinations, data from calibrated flow rate devices, such as glass rotameters, may be used in lieu of incremental dry gas meter readings. Proportional rate calculation procedures must be revised, but acceptability limits remain the same.

During the test run, make periodic adjustments to keep the temperature between (or upstream of) the filters at the proper level. Do not change sampling trains during the test run.

At the end of the test run (see Method 28, Section 6.4.6), turn off the coarse adjust valve, remove the probe 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 4.3.3. 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.

4.3.6 Calculation of Proportional Sampling Rate. Calculate percent proportionality (see Calculations, Section 6) to determine whether the run was valid or another test run should be made.

4.4 Sample Recovery. Begin recovery of the probe and filter samples as described in Method 5, Section 4.2, except that an acetone blank volume of about 50 ml or more may be used.

Treat the samples as follows:

*Container No. 1.* Carefully remove the filter from the primary filter holder and place it in its identified (labeled) 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.* Remove the filter from the second filter holder using the same procedures as described above.

NOTE: The two filters may be placed in the same container for desiccation and weighing. Use the sum of the filter tare weights to determine the sample mass collected.

*Container No. 3.* 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 and filter holders by washing and brushing these components with acetone and placing the wash in a labeled (No. 3) glass container. At least three cycles of brushing and rinsing are necessary.

Between sampling runs, keep brushes clean and protected from contamination.

After all acetone washings and particulate matter have been collected in the sample containers, tighten the lids on the sample containers so that the acetone will not leak out when transferred to the laboratory weighing area. Mark the height of the fluid levels to determine whether leakage occurs during transport. Label the containers clearly to identify contents. Requirements for capping and transport of sample containers are not applicable if sample recovery and analysis occur in the same room.

4.5 Analysis. Record the data required on a sheet such as the one shown in Figure 5G-4. Use the same analytical balance for determining tare weight and final sample weights. Handle each sample container as follows:

*Containers No. 1 and 2.* Leave the contents in the sample containers or transfer the filters and loose particulate to tared glass weighing dishes. Desiccate for no more than 36 hours before the initial weighing, weigh to a constant weight, and report the results to the nearest 0.1 mg. For purposes of this section, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total sample weight (less tare weight), whichever is greater, between two consecutive weighings, with no less than 2 hours between weighings.

*Container No. 3.* Note the level of liquid in the container, and confirm on the analysis sheet whether 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. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1 ml or gravimetrically to within 0.5 g. Transfer the contents to a tared 250 ml or smaller beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report the results to the nearest 0.1 mg.

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

## 5. Calibration

Maintain a laboratory record of all calibrations.

5.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, Section 4, prior to the first certification test and checked semiannually, thereafter. A standard pitot need not be calibrated but shall be inspected and cleaned, if necessary, prior to each certification test.

5.2 Volume Metering System.

5.2.1 Initial and Periodic Calibration. Before its initial use and at least semiannually thereafter, calibrate the volume metering system as described in Method 5, Section 5.3.1, except that the wet test meter with a capacity of 3.0 liters/rev (0.1 ft<sup>3</sup>/rev) may be used. Other liquid displacement systems accurate to within 1 percent, may be used as calibration standards.

Procedures and equipment specified in Method 5, Section 7, for alternative calibration standards, including calibrated dry gas meters and critical orifices, are allowed for calibrating the dry gas meter in the sampling train. A dry gas meter used as a calibration standard shall be recalibrated at least once annually.

5.2.2 Calibration After Use. After each certification or audit test (four or more test runs conducted on a wood heater at the four burn rates specified in Method 28), check calibration of the metering system by performing three calibration runs at a single, intermediate flow rate as described in Method 5, Section 5.3.2.

Procedures and equipment specified in Method 5, Section 7, for alternative calibration standards are allowed for the post-test dry gas meter calibration check.

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

5.3 Temperature Gauges. Use the procedure in Method 2, Section 4.3, to calibrate temperature gauges before the first certification or audit test and at least semiannually, thereafter.

5.4 Leak-Check of Metering System Shown in Figure 5G-1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked prior to initial use and after each certification or audit test. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the procedure described in Method 5, Section 5.6.

Similar leak-checks shall be conducted for other types of metering systems (i.e., without orifice meters).

5.5 Barometer. Calibrate against a mercury barometer before the first certification test and at least semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

5.6 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

## 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.

$B[ws]$  = Water vapor in the gas stream, proportion by volume (assumed to be 0.04).

$c[s]$  = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions,  $g/dsm^3$  ( $g/dscf$ ).

$E$  = Particulate emission rate,  $g/hr$ .

$L[a]$  = Maximum acceptable leakage rate for either a pretest or post-test leak-check, equal to 0.00057  $m^3/min$  (0.02  $cfm$ ) or 4 percent of the average sampling rate, whichever is less.

$L[p]$  = Leakage rate observed during the post-test leak-check,  $m^3/min$  ( $cfm$ ).

$m[a]$  = Mass of residue of acetone blank after evaporation,  $mg$ .

$m[aw]$  = Mass of residue from acetone wash after evaporation,  $mg$ .

$m[n]$  = Total amount of particulate matter collected,  $mg$ .

$M[w]$  = Molecular weight of water, 18.0  $g/g\text{-mole}$  (18.0  $lb/lb\text{-mole}$ ).

$P[bar]$  = Barometric pressure at the sampling site,  $mm\ Hg$  ( $in.\ Hg$ ).

$PR$  = Percent of proportional sampling rate.

$P[s]$  = Absolute gas pressure in dilution tunnel,  $mm\ Hg$  ( $in.\ Hg$ ).

$P[std]$  = Standard absolute pressure, 760  $mm\ Hg$  (29.92  $in.\ Hg$ ).

$Q[sd]$  = Average gas flow rate in dilution tunnel, calculated as in Method 2, Equation 2-10,  $dsm^3/hr$  ( $dscf/hr$ ).

$T[m]$  = Absolute average dry gas meter temperature (see Figure 5G-3),  $^{\circ}K$  ( $^{\circ}R$ ).

$T[mi]$  = Absolute average dry gas meter temperature during each 10-minute interval,  $i$ , of the test run,  $^{\circ}K$  ( $^{\circ}R$ ).

$T[s]$  = Absolute average gas temperature in the dilution tunnel (see Figure 5G 3),  $^{\circ}K$  ( $^{\circ}R$ ).

$T[si]$  = Absolute average gas temperature in the dilution tunnel during each 10 minute interval,  $i$ , of the test run,  $deg.\ K$  ( $deg.\ R$ ).

$T[std]$  = Standard absolute temperature, 293  $deg.\ K$  (528  $deg.\ R$ ).

$V[a]$  = Volume of acetone blank,  $ml$ .

$V[aw]$  = Volume of acetone used in wash,  $ml$ .

V[m] = Volume of gas sample as measured by dry gas meter, dm<sup>3</sup> (dcf).

V[mi] = Volume of gas sample as measured by dry gas meter during each 10-minute interval, i, of the test run, dm<sup>3</sup> (dcf).

V[m(std)] = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dsm<sup>3</sup> (dscf).

V[s] = Average gas velocity in dilution tunnel, calculated by Method 2, Equation 2-9, m/sec (ft/sec). The dilution tunnel dry gas molecular weight may be assumed to be 29 g/g mole (lb/lb mole).

V[si] = Average gas velocity in dilution tunnel during each 10-minute interval, i, of the test run, calculated by Method 2, Equation 2-9, m/sec (ft/sec).

Y = Dry gas meter calibration factor.

DELTA H = Average pressure differential across the orifice meter, if used (see Figure 5G-2), mm H<sub>2</sub>O (in H<sub>2</sub>O).

circle minus = Total sampling time, min.

10 = 10 minutes, length of first sampling period.

13.6 = Specific gravity of mercury.

100 = Conversion to percent.

6.2 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 deg. C, 760 mm Hg or 68 deg. F, 29.92 in. Hg) by using Equation 5G-1. (If no orifice meter is used in sampling train, assume DELTA H = 0 or measure static pressure at dry gas meter outlet.)

$$V[m(std)] = V[m]Y (T[std] / T[m]) X (P[bar] + (DELTA H / 13.6) / P[std]) = K[1]V[m]Y (P[bar] + (DELTA H / 13.6 / T[m])$$
 Eq. 5G-1

where:

K[1] = 0.3858 deg. K/mm Hg for metric units.

= 17.64 deg. R/in. Hg for English units.

NOTE: If L[p] exceeds L[a], Equation 5G-1 must be modified as follows: Replace V[m] in Equation 5G-1 with the expression:

$$[V[m] - (L[p] - L[a]) \text{ circle minus}]$$

6.3 Solvent Wash Blank.

$$m[aw] = (m[a]V[aw] / V[a])$$

Eq. 5G-2

6.4 Total Particulate Weight. Determine the total particulate catch, m[n], from the sum of the weights obtained

from Containers 1, 2, and 3, less the acetone blank (see Figure 5G-4).

#### 6.5 Particulate Concentration.

$$c[s] = (0.001 \text{ g/mg}) \times (m[n] / V[m(\text{std})])$$

Eq. 5G-3

#### 6.6 Particulate Emission Rate.

$$E-c[s]Q[sd]$$

Eq. 5G-4

NOTE: Particulate emission rate results produced using the sampling train described in Section 2 and shown in Figure 5G-1 shall be adjusted for reporting purposes by the following methods adjustment factor:

$$E[\text{adj}] = 1.82 (E)^{0.83}$$

Eq. 5G-5

6.7 Proportional Rate Variation. Calculate PR for each 10-minute interval, *i*, of the test run.

$$PR = \left( \frac{V[m_i]v[s]T[m]T[s_i]}{V[m]V[s]T[s]T[m_i]} \right) \times 100$$

Eq. 5G-6

Alternate calculation procedures for proportional rate variation may be used if other sample flow rate data (e.g., orifice flow meters or rotameters) are monitored to maintain proportional sampling rates. The proportional rate variations shall be calculated for each 10-minute interval by comparing the stack to nozzle velocity ratio for each 10-minute interval to the average stack to nozzle velocity ratio for the test run. Proportional rate variation may be calculated for intervals shorter than 10 minutes with appropriate revisions to Equation 5G-6.

6.8 Acceptable Results. If no more than 10 percent of the PR values for all the intervals exceed 90 percent < PR < 110 percent, and if no PR value for any interval exceeds 80 percent < PR < 120 percent, the results are acceptable. If the PR values for the test run are judged to be unacceptable, report the test run emission results, but do not include the results in calculating the weighted average emission rate, and repeat the test run.

### 7. Alternative Sampling and Analysis Procedure

7.1 Method 5H Sampling Train. The sampling and analysis train and procedures described in Method 5H, Sections 2.1, 3.1, 3.2, 5.1, 5.2.3, 5.3, and 5.6 may be used in lieu of similar sections in Method 5G. Operation of the Method 5H sampling train in the dilution tunnel is as described in Section 4.3.5 of this method. Filter temperatures and condenser conditions are as described in Method 5H. No methods adjustment factor as described in Equation 5G-5, Section 6.6, is to be applied to the particulate emission rate data produced by this alternative method.

7.2 Dual Sampling Trains. The tester may operate two sampling trains simultaneously at sample flow rates other than that specified in Section 4.3.5 provided the following specifications are met.

7.2.1 Sampling Train. The sampling train configuration shall be the same as specified in Section 2.1, except the probe, filter, and filter holder need not be the same sizes as specified in the applicable sections. Filter holders of

plastic materials such as Nalgene or polycarbonate materials may be used (the Gelman 1119 filter holder has been found suitable for this purpose). With such materials, it is recommended not to use solvents in sample recovery. The filter face velocity shall not exceed 150 mm/sec (30 ft/min) during the test run. The dry gas meter shall be calibrated for the same flow rate range as encountered during the test runs. Two separate, complete sampling trains are required for each test run.

7.2.2 Probe Location. Locate the two probes in the dilution tunnel at the same level (see Section 2.2.3). Two sample ports are necessary. Locate the probe inlets within the 50 mm (2 in.) diameter centroidal area of the dilution tunnel no closer than 25 mm (1 in.) apart.

7.2.3 Sampling Train Operation. Operate the sampling trains as specified in Section 4.3.5, maintaining proportional sampling rates and starting and stopping the two sampling trains simultaneously. The pitot values as described in Section 4.2.2 shall be used to adjust sampling rates in both sampling trains.

7.2.4 Recovery and Analysis of Sample. Recover and analyze the samples from the two sampling trains separately, as specified in Sections 4.4 and 4.5.

For this alternative procedure, the probe and filter holder assembly may be weighed without sample recovery (use no solvents) described above in order to determine the sample weight gains. For this approach, weigh the clean, dry probe and filter holder assembly upstream of the front filter (without filters) to the nearest 0.1 mg to establish the tare weights. The filter holder section between the front and second filter need not be weighed. At the end of the test run, carefully clean the outside of the probe, cap the ends, and identify the sample (label). Remove the filters from the filter holder assemblies as described for containers Nos. 1 and 2 above. Reassemble the filter holder assembly, cap the ends, identify the sample (label), and transfer all the samples to the laboratory weighing area for final weighing. Descriptions of capping and transport of samples are not applicable if sample recovery and analysis occur in the same room.

For this alternative procedure, filters may be weighed directly without a petri dish. If the probe and filter holder assembly are to be weighed to determine the sample weight, rinse the probe with acetone to remove moisture before desiccating prior to the test run. Following the test run, transport the probe and filter holder to the dessicator, and uncap the openings of the probe and the filter holder assembly. Desiccate no more than 36 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

7.25 Calculations. Calculate an emission rate (Section 6.6) for the sample from each sampling train separately and determine the average emission rate for the two values. The two emission rates shall not differ by more than 7.5 percent from the average emission rate, or 7.5 percent of the weighted average emission rate limit in the applicable standard, whichever is greater. If this specification is not met, the results are unacceptable. Report the results, but do not include the results in calculating the weighted average emission rate. Repeat the test run until acceptable results are achieved, report the average emission rate for the acceptable test run, and use the average in calculating the weighted average emission rate.

## 8. Bibliography

1. Same as for Method 5, citations 1 through 11, with the addition of the following:
2. Oregon Department of Environmental Quality Standard Method for Measuring the Emissions and Efficiencies of Woodstoves, June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.
3. American Society for Testing Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E-6 Proposal P 180. August 1986.

Figure 5G-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

Figure 5G-2. Suggested construction details of the dilution tunnel.

[SEE FIGURE IN ORIGINAL]

Figure 5G-3. Particulate Field data sheet.

[SEE FIGURE IN ORIGINAL]

Stove §

Date

Run No.

Filter Nos.

Liquid lost during transport, ml

Acetone blank volume, ml

Acetone wash volume, ml

Acetone blank concentration, mg/mg

Acetone wash blank, mg

Container No.	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1			
2			
3			
Total			
Less acetone blank			
Weight of particulate matter			

## STACK MOISTURE MEASUREMENT DATA

(OPTIONAL)

Volume of liquid water

	collected	
Impinger		Silica gel
volume,		weight, g
ml		

Final  
 Initial  
 Liquid collected  
 Total volume  
 collected

g ml ml

n1 Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

Increase, g / (1 g/ml) = Volume water, ml

Figure 5G-4. Analysis data sheet.

## METHOD 5H -- DETERMINATION OF PARTICULATE EMISSIONS FROM WOOD HEATERS FROM A STACK LOCATION

### *Applicability and Principle*

1.1 Applicability. This method is applicable for the determination of particulate matter and condensable emissions from wood heaters.

1.2 Principle. Particulate matter is withdrawn proportionally from the wood heater exhaust and is collected on two glass fiber filters separated by impingers immersed in an ice bath. The first filter is maintained at a temperature of no greater than 120 deg. C (248 deg. F). The second filter and the impinger system are cooled such that the exiting temperature of the gas is no greater than 20 deg. C (68 deg. F). The particulate mass collected in the probe, on the filters, and in the impingers is determined gravimetrically after removal of uncombined water.

### *2. Apparatus*

2.1 Sampling Train. The sampling train configuration is shown in Figure 5H-1. APTD-0576 is suggested for operating and maintenance procedures. The train consists of the following components:

2.1.1 Probe Nozzle. (Optional) Same as Method 5, Section 2.1.1. A straight sampling probe without a nozzle is an acceptable alternative.

2.1.2 Probe Liner. Same as Method 5, Section 2.1.2, except that the maximum length of the sample probe shall be 0.6 m (2 ft) and probe heating is optional.

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

2.1.4 Filter Holders. Two each of borosilicate glass, with a glass frit or stainless steel filter support and a silicone rubber, Teflon, or Viton gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The front filter holder shall be attached immediately at the outlet of the probe and prior to the first impinger. The second filter holder shall be attached on the outlet of the third impinger and prior to the inlet of the fourth (silica gel) impinger.

NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

2.1.5 Filter Heating System. Same as Method 5, Section 2.1.6.

2.1.6 Condenser. Same as Method 5, Section 2.1.7, used to collect condensible materials and determine the stack gas moisture content.

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

2.1.8 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

2.2 Stack Flow Rate Measurement System. A schematic of an example test system is shown in Figure 5H-2. The flow rate measurement system consists of the following components:

2.2.1 Sample Probe. A glass or stainless steel sampling probe.

2.2.2 Gas Conditioning System. A high density filter to remove particulate matter and a condenser capable of lowering the dew point of the gas to less than 5 deg. C (40 deg. F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

2.2.3 Pump. An inert (i.e., Teflon or stainless steel heads) sampling pump capable of delivering more than the total amount of sample required in the manufacturer's instructions for the individual instruments. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls) shall be provided at the analyzer. The requirements for measuring and controlling the analyzer flow rate are not applicable if data are presented that demonstrate the analyzer is insensitive to flow variations over the range encountered during the test.

2.2.4 CO Analyzer. Any analyzer capable of providing a measure of CO in the range of 0 to 10 percent by volume at least once every 10 minutes.

2.2.5 CO<sub>2</sub> Analyzer. Any analyzer capable of providing a measure of CO<sub>2</sub> in the range of 0 to 25 percent by volume at least once every 10 minutes.

NOTE: Analyzers with ranges less than those specified above may be used provided actual concentrations do not exceed the range of the analyzer.

2.2.6 Manifold. A sampling tube capable of delivering the sample gas to two analyzers and handling an excess of the total amount used by the analyzers. The excess gas is exhausted through a separate port.

2.2.7 Recorders (optional). To provide a permanent record of the analyzer outputs.

2.3 Proportional Gas Flow Rate System. To monitor stack flow rate changes and provide a measurement that can be used to adjust and maintain particulate sampling flow rates proportional to the stack flow rate. A schematic of the proportional flow rate system is shown in Figure 5H-2 and consists of the following components:

2.3.1 Tracer Gas Injection System. To inject a known concentration of SO<sub>2</sub> into the flue. The tracer gas injection system consists of a cylinder of SO<sub>2</sub>, a gas cylinder regulator, a stainless steel needle valve or flow controller, a nonreactive (stainless steel and glass) rotameter, and an injection loop to disperse the SO<sub>2</sub> evenly

in the flue.

2.3.2 Sample Probe. A glass or stainless steel sampling probe.

2.3.3 Gas Conditioning System. A combustor as described in Method 16A, Sections 2.1.5 and 2.1.6, followed by a high density filter to remove particulate matter, and a condenser capable of lowering the dew point of the gas to less than 5 deg. C (40 deg. F). Desiccant, such as Drierite, may be used to dry the sample gas. Do not use silica gel.

2.3.4 Pump. As described in Section 2.2.3.

2.3.5 SO<sub>2</sub> Analyzer. Any analyzer capable of providing a measure of the SO<sub>2</sub> concentration in the range of 0 to 1,000 ppm by volume (or other range necessary to measure the SO<sub>2</sub> concentration) at least once every 10 minutes.

2.3.6 Recorder (optional). To provide a permanent record of the analyzer outputs.

NOTE: Other tracer gas systems, including helium gas systems, are allowed for determining instantaneous proportional sampling rates.

2.4 Sample Recovery. Probe liner and probe nozzle brushes, wash bottles, sample storage containers, petri dishes, graduated cylinder or balance, plastic storage containers, funnel and rubber policeman, as described in Method 5, Sections 2.2.1 through 2.2.8, respectively, are needed.

2.5 Analysis. Weighing dishes, desiccator, analytical balance, beakers (250 ml or less), hygrometer or psychrometer, and temperature gauge as described in Method 5, Sections 2.3.1 through 2.3.7, respectively, are needed. In addition, a separatory funnel, glass or Teflon, 500 ml or greater, is needed.

### *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. Gelman A/E 61631 filters have been found acceptable for this purpose.

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). Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Same as Method 5, Section 3.1.5.

3.2 Sample Recovery. Same as Method 5, Section 3.2.

3.3 Cylinder Gases. For the purposes of this procedure, span value is defined as the upper limit of the range specified for each analyzer as described in Section 2.2 or 2.3. If an analyzer with a range different from that specified in this method is used, the span value shall be equal to the upper limit of the range for the analyzer used (see NOTE in Section 2.2.5).

3.3.1 Calibration Gases. The calibration gases for the CO<sub>2</sub>, CO and SO<sub>2</sub> analyzers shall be CO<sub>2</sub>, CO, or SO<sub>2</sub>, as appropriate, in N<sub>2</sub>. CO<sub>2</sub> and CO calibration gases may be combined in a single cylinder.

There are two alternatives for checking the concentrations of the calibration gases. (a) The first is to use calibration gases that are documented traceable to National Bureau of Standards Reference Materials. Use *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors* (Protocol Number 1) that is available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Mail Drop 77, Environmental Protection Agency, Research Triangle Park, North Carolina 27711. Obtain a certification from the gas manufacturer that the protocol was followed. These calibration gases are not to be analyzed with the test methods. (b) The second alternative is to use calibration gases not prepared according to the protocol. If this alternative is chosen, within 6 months prior to the certification test, analyze each of the CO<sub>2</sub> and CO calibration gas mixtures in triplicate using Method 3, and within 1 month prior to the certification test, analyze SO<sub>2</sub> calibration gas mixtures using Method 6. For the low-level, mid-level, or high-level gas mixtures, each of the individual SO<sub>2</sub> analytical results must be within 10 percent (or 10 ppm, whichever is greater) of the triplicate set average; CO<sub>2</sub> and CO test results must be within 0.5 percent CO<sub>2</sub> and CO; otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate test method results is within 5 percent for SO<sub>2</sub> gas (or 0.5 percent CO<sub>2</sub> and CO for the CO<sub>2</sub> and CO gases) of the calibration gas manufacturer's tag values, use the tag value; otherwise, conduct at least three additional test method analyses until the results of six individual SO<sub>2</sub> runs (the three original plus three additional) agree within 10 percent (or 10 ppm, whichever is greater) of the average (CO<sub>2</sub> and CO test results must be within 0.5 percent). Then use this average for the cylinder value. Four calibration gas levels are required as specified below:

3.3.1.1 High-level Gas. A gas concentration that is equivalent to 80 to 90 percent of the span value.

3.3.1.2 Mid-level Gas. A gas concentration that is equivalent to 45 to 55 percent of the span value.

3.3.1.3 Low-level Gas. A gas concentration that is equivalent to 20 to 30 percent of the span value.

3.3.1.4 Zero Gas. A gas concentration of less than 0.25 percent of the span value. Purified air may be used as zero gas for the CO<sub>2</sub>, CO, and SO<sub>2</sub> analyzers.

3.3.2 SO<sub>2</sub> Injection Gas. A known concentration of SO<sub>2</sub> in N<sub>2</sub>. The concentration must be at least 2 percent SO<sub>2</sub> with a maximum of 100 percent SO<sub>2</sub>. The cylinder concentration shall be certified by the manufacturer to be within 2 percent of the specified concentration.

3.4 Analysis. Three reagents are required for the analysis:

3.4.1 Acetone. Same as 3.2.

3.4.2 Dichloromethane (Methylene Chloride). Reagent grade, < 0.001 percent residue in glass bottles.

3.4.3 Desiccant. Anhydrous calcium sulfate, calcium chloride, or silica gel, indicating type.

4. *Gas Measurement System Performance Specifications.*

4.1 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration. The response time for each analyzer and gas conditioning system shall be no more than 2 minutes.

4.2 Zero Drift. The zero drift value for each analyzer shall be less than 2.5 percent of the span value over the period of the test run.

4.3 Calibration Drift. The calibration drift value measured with the mid-level calibration gas for each analyzer shall be less than 2.5 percent of the span value over the period of the test run.

4.4 Resolution. The resolution of the output for each analyzer shall be 0.5 percent of span value or less.

4.5 Calibration Error. The linear calibration curve produced using the zero and mid-level calibration gases shall predict the actual response to the low-level and high-level calibration gases within 2 percent of the span value.

## 5. Procedure

### 5.1 Pretest Preparation.

5.1.1 Filter and Desiccant. Same as Method 5, Section 4.1.1.

5.1.2 Sampling Probe and Nozzle. The sampling location for the particulate sampling probe shall be 2.45 +/- 0.15 m (8 +/- 0.5 ft) above the platform upon which the wood heater is placed (i.e., the top of the scale).

Select a nozzle, if used, sized for the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain proportional sampling rates. During the run, do not change the nozzle size.

Select a suitable probe liner and probe length to effect minimum blockage.

5.1.3 Preparation of Particulate Sampling Train. During preparation and assembly of the particulate 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 surgical gloves, place one labeled (identified) and weighed filter in each of the filter holders. Be sure that each of the filters is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filters for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct.

Set up the train as in Figure 5H 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.

Place crushed ice around the the impingers.

### 5.1.4 Leak-Check Procedures.

5.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, conduct the leak-check as described in Method 5, Section 4.1.4.1, except that a vacuum of 130 mm Hg (5 in. Hg) may be used instead of 380 mm Hg (15 in. Hg).

5.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, conduct a leak-check as described in Method 5, Section 4.1.4.2.

5.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures described in Method 5, Section 4.1.4.3, except that a vacuum of 130 mm Hg (5 in. Hg) or the greatest vacuum measured during the test run, whichever is greater, may be used instead of 380 mm Hg (15 in. Hg).

5.1.5 Tracer Gas Procedure. A schematic of the tracer gas injection and sampling systems is shown in Figure 5H-2.

5.1.5.1 SO<sub>2</sub> Injection Probe. Install the SO<sub>2</sub> injection probe and dispersion loop in the stack at a location 2.8 +/- 0.15 m (9.5 +/- 0.5 ft) above the sampling platform.

5.1.5.2 SO<sub>2</sub> Sampling Probe. Install the SO<sub>2</sub> sampling probe at the centroid of the stack at a location 4 +/- 0.15 m (13.5 +/- 0.5 ft) above the sampling platform.

5.1.6 Flow Rate Measurement System. A schematic of the flow rate measurement system is shown in Figure 5H-2. Locate the flow rate measurement sampling probe at the centroid of the stack at a location 2.3 +/- 0.3 m (7.5 +/- 1 ft) above the sampling platform.

5.2 Test Run Procedures. The start of the test run is defined as in Method 28, Section 6.4.1.

5.2.1 Tracer Gas Procedure. Within 1 minute after closing the wood heater door at the start of the test run, meter a known concentration of SO<sub>2</sub> tracer gas at a constant flow rate into the wood heater stack. Monitor the SO<sub>2</sub> concentration in the stack, and record the SO<sub>2</sub> concentrations at 10-minute intervals or more often at the option of the tester. Adjust the particulate sampling flow rate proportionally to the SO<sub>2</sub> concentration changes using Equation 5H-6 (e.g., the SO<sub>2</sub> concentration at the first 10-minute reading is measured to be 100 ppm; the next 10 minute SO<sub>2</sub> concentration is measured to be 75 ppm: the particulate sample flow rate is adjusted from the initial 0.15 cfm to 0.20 cfm). A check for proportional rate variation shall be made at the completion of the test run using Equation 5H-10.

5.2.2 Volumetric Flow Rate Procedure. Apply stoichiometric relationships to the wood combustion process in determining the exhaust gas flow rate as follows:

5.2.2.1 Test Fuel Charge Weight. Record the test fuel charge weight in kilograms (wet) as specified in Method 28, Section 6.4.2. The wood is assumed to have the following weight percent composition: 51 percent carbon, 7.3 percent hydrogen, 41 percent oxygen. Record the wood moisture for each wood charge as described in Method 28, Section 6.2.5. The ash is assumed to have negligible effect on associated C, H, O concentrations after the test burn.

5.2.2.2 Measured Values. Record the CO and CO<sub>2</sub> concentrations in the stack on a dry basis every 10 minutes during the test run or more often at the option of the tester. Average these values for the test run. Use as a mole fraction (e.g., 10 percent CO<sub>2</sub> is recorded as 0.10) in the calculations to express total flow Equation 5H-7.

5.2.3 Particulate Train Operation. For each run, record the data required on a data sheet such as the one shown in Figure 5H-3. 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 as indicated on Figure 5H-3 at least once each 10 minutes during the test run.

Remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the probe is properly positioned. Position the nozzle, if used, facing into gas stream, or the probe tip in the 50 mm (2 in.) centroidal area of the stack.

Be careful not to bump the probe tip into the stack wall when removing or inserting the probe through the porthole; this minimizes the chance of extracting deposited material.

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

Begin sampling at the start of the test run as defined in Method 28, Section 6.4.1, start the sample pump, and adjust the sample flow rate to between 0.003 and 0.015 m<sup>3</sup>/min (0.1 and 0.5 cfm). Adjust the sample flow rate proportionally to the stack flow during the test run (Section 5.2.1), and maintain a proportional sampling rate (within 10 percent of the desired value) and a filter holder temperature no greater than 120 deg. C (248 deg. F).

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level. Add more ice to the impinger box and, if necessary, salt to maintain a temperature of less than 20 deg. C (68 deg. F) at the condenser/silica gel outlet.

If the pressure drop across the filter becomes too high, making sampling difficult to maintain, either filter may be replaced during 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 5.1.4.2). The total particulate weight shall include the summation of all filter assembly catches. The total time for changing sample train components shall not exceed 10 minutes. No more than one component change is allowed for any test run.

At the end of the test 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 5.1.4.3.

**5.3 Sample Recovery.** Begin recovery of the probe and filter sample as described in Method 5, Section 4.2, except that an acetone blank volume of about 50 ml may be used. Treat the samples as follows:

*Container No. 1.* Carefully remove the filter from the front 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 and label the container.

*Container No. 2.* Remove the filter from the back filter holder using the same procedures as described above.

*Container No. 3.* Same as Method 5, Section 4.2 for Container No. 2. except that descriptions of capping and sample transport are not applicable if sample recovery and analysis occur in the same room.

*Container No. 4.* Treat the impingers as follows: 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.

Transfer the water from the first, second and third impingers to a glass container. Tighten the lid on the sample container so that water will not leak out. Rinse impingers and graduated cylinder, if used, with acetone three

times or more. Avoid direct contact between the acetone and any stopcock grease or collection of any stopcock grease in the rinse solutions. Add these rinse solutions to sample Container No. 3.

Whenever possible, containers should be transferred in such a way that they remain upright at all times. Descriptions of capping and transport of samples are not applicable if sample recovery and analysis occur in the same room.

*Container No. 5.* 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, follow the procedure for Container No. 5 in Section 5.4.

5.4 Analysis. Record the data required on a sheet such as the one shown in Figure 5H-4. Handle each sample container as follows:

*Containers No. 1 and 2.* Leave the contents in the shipping container or transfer both of the filters and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for no more than 36 hours. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 5.6, 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 2 hours between weighings.

*Container No. 3.* Note the level of liquid in the container and confirm on the analysis sheet whether 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. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1 ml or gravimetrically to within 0.5 g. Transfer the contents to a tared 250-ml or smaller beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report the results to the nearest 0.1 mg.

*Container No. 4.* Note the level of liquid in the container and confirm on the analysis sheet whether 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. Determination of sample leakage is not applicable if sample recovery and analysis occur in the same room. Measure the liquid in this container either volumetrically to within 1 ml or gravimetrically to within 0.5 g. Transfer the contents to a 500 ml or larger separatory funnel. Rinse the container with water, and add to the separatory funnel. Add 25 ml of dichloromethane to the separatory funnel, stopper and vigorously shake 1 minute, let separate and transfer the dichloromethane (lower layer) into a tared beaker or evaporating dish. Repeat twice more. It is necessary to rinse the Container No. 4 with dichloromethane. This rinse is added to the impinger extract container. Transfer the remaining water from the separatory funnel to a tared beaker or evaporating dish and evaporate to dryness at 220 deg. F (105 deg. C). Desiccate and weigh to a constant weight. Evaporate the combined impinger water extracts at ambient temperature and pressure. Desiccate and weigh to a constant weight. Report both results to the nearest 0.1 mg.

*Container No. 5.* Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

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

*"Dichloromethane" Container.* Measure 75 ml of dichloromethane in this container and treat it the same as the

"acetone blank."

*"Water Blank" Container.* Measure 200 ml water into this container either volumetrically or gravimetrically. Transfer the water to a tared 250-ml beaker and evaporate to dryness at 105 deg. C (221 deg. F). Desiccate and weigh to a constant weight.

## 6. Calibration

Maintain a laboratory record of all calibrations.

### 6.1 Volume Metering System.

6.1.1 Initial and Periodic Calibration. Before the first certification or audit test and at least semiannually, thereafter, calibrate the volume metering system as described in Method 5G, Section 5.2.1.

6.1.2 Calibration After Use. Same as Method 5G, Section 5.2.2.

6.1.3 Acceptable Variation in Calibration. Same as Method 5G, Section 5.2.3.

6.2 Probe Heater Calibration. (Optional) The probe heating system shall be calibrated before the first certification or audit test. Use the procedure described in Method 5, Section 5.4.

6.3 Temperature Gauges. Use the procedure in Method 2, Section 4.3, to calibrate in-stack temperature gauges before the first certification or audit test and semiannually, thereafter.

6.4 Leak-Check of Metering System Shown in Figure 5H-1. That portion of the sampling train from the pump to the orifice meter shall be leak-checked after each certification or audit test. Use the procedure described in Method 5, Section 5.6.

6.5 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually, thereafter. If a mercury barometer is used, no calibration is necessary. Follow the manufacturer's instructions for operation.

6.6 SO<sub>2</sub> Injection Rotameter. Calibrate the SO<sub>2</sub> injection rotameter system with a soap film flowmeter or similar direct volume measuring device with an accuracy of +/- 2 percent. Operate the rotameter at a single reading for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within 5 percent, average the three flow rates, mark the rotameter at the calibrated setting, and use the calibration flow rate as the SO<sub>2</sub> injection flow rate during the test run. Repeat the rotameter calibration before the first certification test and semiannually, thereafter.

6.7 Analyzer Calibration Error Check. Conduct the analyzer calibration error check prior to each certification test.

6.7.1 Calibration Gas Injection. After the flow rate measurement system and the tracer gas measurement system have been prepared for use (Sections 5.1.5.2 and 5.1.6), introduce zero gases and then the mid-level calibration gases for each analyzer. Set the analyzers' output responses to the appropriate levels. Then introduce the low-level and high-level calibration gases, one at a time, for each analyzer. Record the analyzer responses.

6.7.2 Acceptability Values. If the linear curve for any analyzer determined from the zero and mid-level calibration gases' responses does not predict the actual responses of the low-level and high-level gases within 2 percent of the span value, the calibration of that analyzer shall be considered invalid. Take corrective measures on the measurement system before repeating the calibration error check and proceeding with the test runs.

6.8 Measurement System Response Time. Introduce zero gas at the calibration gas valve into the flow rate measurement system and the tracer gas measurement system until all readings are stable. Then, quickly switch to introduce the mid-level calibration gas at the calibration value until a stable value is obtained. A stable value is equivalent to a change of less than 1 percent of span value for 30 seconds. Record the response time. Repeat the procedure three times. Conduct the response time check for each analyzer separately before its initial use and at least semiannually thereafter.

6.9 Measurement System Drift Checks. Immediately prior to the start of each test run (within 1 hour of the test run start), introduce zero and mid-level calibration gases, one at a time, to each analyzer through the calibration valve. Adjust the analyzers to respond appropriately. Immediately following each test run (within 1 hour of the end of the test run), or if adjustments to the analyzers or measurement systems are required during the test run, reintroduce the zero- and mid-level calibration gases and record the responses, as described above. Make no adjustments to the analyzers or the measurement system until after the drift checks are made.

If the difference between the analyzer responses and the known calibration gas values exceed the specified limits (Sections 4.2 and 4.3), the test run will be considered invalid and shall be repeated following corrections to the measurement system. Alternatively, recalibrate the measurement system and recalculate the measurement data. Report the test run results using both the initial and final calibration data.

6.10 Analytical Balance. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first certification test and semiannually, thereafter. Before each certification test, audit the balance by weighing at least one calibration weight (class F) that corresponds to 50 to 150 percent of the weight of one filter. If the scale cannot reproduce the value of the calibration weight to within 0.1 mg, conduct the multipoint calibration before use.

## 7. 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.

### 7.1 Nomenclature.

a = Sample flow rate adjustment factor.

BR = dry wood burn rate, kg/hr (lb/hr), from Method 28, Section 8.3.

B[ws] = Water vapor in the gas stream, proportion by volume.

c[s] = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dsm<sup>3</sup> (g/dscf).

E = Particulate emission rate, g/hr.

DELTAH = Average pressure differential across the orifice meter (see Figure 5H-1), mm H<sub>2</sub>O (in. H<sub>2</sub>O).

L[a] = Maximum acceptable leakage rate for either a post-test leak check or for a leak-check following a component change; equal to 0.00057 m<sup>3</sup>/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L[1] = Individual leakage rate observed during the leak-check conducted before a component change,

$m_{3}/\text{min}$  (cfm).

$L[p]$  = Leakage rate observed during the post-test leak-check,  $m_{3}/\text{min}$  (cfm).

$m[n]$  = Total amount of particulate matter collected, mg.

$m[a]$  = Mass of residue of solvent after evaporation, mg.

$N[c]$  = Gram atoms of carbon/gram of dry fuel (lb/lb), equal to 0.0425.

$N[T]$  = Total dry moles of exhaust gas/Kg of dry wood burned, g-moles/kg (lb-moles/lb).

PR = Percent of proportional sampling rate.

$P[\text{bar}]$  = Barometric pressure at the sampling site, mm Hg (in. Hg).

$P[\text{std}]$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

$Q[\text{sd}]$  = Total gas flow rate,  $\text{dm}^3/\text{hr}$  (dscf/hr).

$Q[T]$  = Flow of tracer gas, liters/min.

$S[i]$  = Concentration measured at the  $\text{SO}_2$  analyzer for the "i<sup>th</sup>" 10 minute interval, ppm.

$S[1]$  = Concentration measured at the  $\text{SO}_2$  analyzer for the first 10-minute interval, ppm.

$T[1]$  = Absolute average stack gas temperature for the first 10-minute interval, deg. K (deg. R).

$T[i]$  = Absolute average stack gas temperature at the "i<sup>th</sup>" 10-minute interval, deg. K (deg. R).

$T[m]$  = Absolute average dry gas meter temperature (see Figure 5H-3), deg. K (deg. R).

$T[\text{std}]$  = Standard absolute temperature, 293 deg. K (528 deg. R).

$V[a]$  = volume of solvent blank, ml.

$V[\text{aw}]$  = Volume of solvent used in wash, ml.

$V[\text{lc}]$  = Total volume of liquid collected in impingers and silica gel (see Figure 5H-4), ml.

$V[m]$  = Volume of gas sample as measured by dry gas meter,  $\text{dm}^3$  (dcf).

$V[m(\text{std})]$  = Volume of gas sample measured by the dry gas meter, corrected to standard conditions,  $\text{dm}^3$  (dscf).

$V[m(\text{std})]$  = Volume of gas sample measured by the dry gas meter during the first 10-minute interval, corrected to standard conditions,  $\text{dm}^3$  (dscf).

$V[m(\text{std})]$  = Volume of gas sample measured by the dry gas meter during the "i<sup>th</sup>" 10-minute interval,  $\text{dm}^3$  (dscf).

$V[w(\text{std})]$  = Volume of water vapor in the gas sample, corrected to standard conditions,  $\text{sm}^3$  (scf).

W[a] = Weight of residue in solvent wash, mg.

Y = Dry gas meter calibration factor.

Y[co] = Measured mole fraction of CO (dry), average from Section 5.2.2.2, g/g-mole (lb/lb-mole).

Y[CO<2>] = Measured mole fraction of CO[2] (dry), average from Section 5.2.2.2, g/g-mole (lb/lb-mole).

Y[HC] = Assumed mole fraction of HC (dry), g/g-mole (lb/lb-mole);

= 0.0088 for catalytic wood heaters;

= 0.0132 for non-catalytic wood heaters;

= 0.0080 for pellet-fired wood heaters.

10 = Length of first sampling period, minutes.

13.6 = Specific gravity of mercury.

100 = Conversion to percent.

circle minus = Total sampling time, min.

circle minus[1] = Sampling time interval, from the beginning of a run until the first component change, min.

7.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5H-3).

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

$$V[m(std)] = V[m]Y T[std] / T[m] (P[bar] + DELTAH/ 13.6 / P[std]) = K[l]V[m]Y (P[bar] + (DELTAH / 13.6) / T[m]) \text{ Eq. 5H-1}$$

where:

K[j1] = 0.3858 deg. K/m. Hg for metric units.

= 17.64 deg. R/in. Hg for English units.

NOTE: Equation 5H-1 can be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-leak leak-check or leak-check conducted before a component change) exceeds L[a].

If L[p] exceeds L[a], Equation 5H-1 must be modified as follows:

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

$$[V[m]-(L[p]-L[a])\text{circle minus}]$$

(b) Case II. One component change made during the sampling run. In this case, replace V[m] in Equation 5H-1

by the expression:

$$V[m] - (L[1] - L[a])$$

and substitute only for those leakage rates ( $L[1]$  or  $L[p]$ ) which exceed  $L[a]$ .

#### 7.4 Volume of Water Vapor.

$$V[w(\text{std})] = K[2]V[lc] \text{ Eq. 5H-2}$$

where:

$$K[2] = 0.001333 \text{ m}^3/\text{ml} \text{ for metric units}$$

$$= 0.04707 \text{ ft}^3/\text{ml} \text{ for English units.}$$

#### 7.5 Moisture Content.

$$B[ws] = (V[w(\text{std})] / V[m(\text{std})] + V[w(\text{std})])$$

Eq. 5H-3

#### 7.6 Solvent Wash Blank.

$$W[a] = (m[a]V[aw] / V[a])$$

Eq. 5H-4

7.7 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1, 2, 3, and 4 less the appropriate solvent blanks (see Figure 5H-4).

NOTE: Refer to Method 5, Section 4.1.5 to assist in calculation of results involving two filter assemblies.

#### 7.8 Particulate Concentration

$$c[s] = (0.001 \text{ g/mg}) (m[n]/V[m(\text{std})])$$

Eq. 5H-5

#### 7.9 Sample Flow Rate Adjustment.

$$a = S[1] / S[1]$$

Eq. 5H-6

#### 7.10 Carbon Balance for Total Moles of Exhaust Gas (dry)/Kg of Wood Burned in the Exhaust Gas.

$$N[T] = (K[3]N[C] / (Y[CO_2] + Y[CO] + Y[HC]))$$

Eq. 5H-7

where:

$K[3] = 1000 \text{ g/kg}$  for metric units.

$K[3] = 1.0 \text{ lb/lb}$  for English units.

NOTE: the  $\text{NO}[x]/\text{SO}[x]$  portion of the gas is assumed to be negligible.

7.11 Total Stack Gas Flow Rate.

$$Q[\text{sd}] = K[4]N[\text{T}]BR$$

Eq. 5H-8

where:

$K[4] = 0.02406$  for metric units,  $\text{dsm}^3/\text{g-mole}$ .

$= 384.8$  for English units,  $\text{dscf/lb-mole}$ .

7.12 Particulate Emission Rate.

$$E = c[\text{s}]Q[\text{sd}]$$

Eq. 5H-9

7.13 Proportional Rate Variation. Calculate PR for each 10-minute interval,  $i$ , of the test run.

$$PR = \left( \frac{S[i]V[\text{m}(\text{std})]}{10 \sum_{i=1}^n S[i]V[\text{mi}(\text{std})]} \right) \times 100$$

Eq. 5H-10

7.14 Acceptable Results. If no more than 15 percent of the PR values for all the intervals exceed 90 percent  $< PR < 110$  percent, and if no PR value for any interval exceeds 75  $< PR < 125$  percent, the results are acceptable. If the PR values for the test runs are judged to be unacceptable, report the test run emission results, but do not include the test run results in calculating the weighted average emission rate, and repeat the test.

## 8. Bibliograph

1. Same as for Method 5, citations 1 through 11, with the addition of the following:
2. Oregon Department of Environmental Quality Standard Method for Measuring the emissions and efficiencies of Woodstoves, July 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.
3. American Society for Testing Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-fired Closed Combustion-Chamber Heating Appliances. E-6 Proposal P 180. August 1986.

Figure 5H-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

Figure 5H-2. Test system schematic for Method 5H.

[SEE FIGURE IN ORIGINAL]

Figure 5H-3. Data sheet.

[SEE FIGURE IN ORIGINAL]

Figure 5H-4. Analysis data sheet.

[SEE FIGURE IN ORIGINAL]

## 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<sub>2</sub>/m<sup>3</sup> (2.12 X 10<sup>-7</sup> lb/ft<sup>3</sup>). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m<sup>3</sup> of SO<sub>2</sub> 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<sup>3</sup>.

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<sub>2</sub> analysis. When samples are being taken from a gas stream with high concentrations of very fine 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<sub>2</sub> 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 the presence of white particulate matter in the probe and isopropanol bubbler), the alternative procedures in Section 7.2 shall be used.

Figure 6-1. SO<sub>2</sub> sampling train.

[SEE FIGURE IN ORIGINAL]

### 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<sub>2</sub> 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<sub>2</sub> 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 out-stack) 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<sub>2</sub>.

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 deg. C (2 deg. 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 deg. C (350 deg. 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 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 deg. C (5.4 deg 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  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present. Unless otherwise specified, this water shall be used throughout this method.

3.1.2 Isopropanol, 80 percent. Mix 80 ml of isopropanol with 20 ml of 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 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 water (30 ml is needed per sample). Prepare fresh daily.

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

### 3.2 Sample Recovery.

3.2.1 Water. Same as in Section 3.1.1.

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

3.3 Analysis.

3.3.1 Water. Same as in Section 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 water.

3.3.4 Barium Perchlorate Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [Ba(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O] 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 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 enforcement agency at least 30 days prior to the test date to allow sufficient time for sample delivery).

3.3.7 Hydrochloric Acid (HCl) Solution, 0.1 N (for use in Section 7.2). Carefully pipette 8.6 ml of concentrated HCl into a 1-liter volumetric flask containing water. Dilute to volume with mixing.

#### 4. Procedure

##### 4.1 Sampling.

4.1.1 Preparation of Collection Train. Measure 15 ml of 80 percent isopropanol into the midjet bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midjet impingers. Leave the final midjet 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 vacuum 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 inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either 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 drying 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 Administrator, 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, temperatures 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 temperature of the gases leaving the last impinger at 20 deg. C (68 deg. 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<sub>2</sub>O<sub>2</sub>. 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 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 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 thiorin 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<sub>2</sub>/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 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 shall remain stable for at least 30 seconds. Carefully release the vacuum 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 of the drying tube. 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<sub>2</sub>] = 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, deg. K (deg. R).

T[std] = Standard absolute temperature, 293 deg. K (528 deg. 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.

$$V[m](std) = V[m] \times Y \times (T[std] / T[m]) \times (P[bar] / P[std]) = K[1] \times Y \times (V[m] \times P[bar] / T[m])$$

Equation 6-1

Where:

K[1] = 0.3858 deg. K/mm Hg for metric units.

= 17.64 deg. R/in. Hg for English units.

### 6.3 Sulfur Dioxide Concentration.

$$C[\text{SO}_2] = K[3] \times ((V[t] - V[tb]) \times N \times (V[\text{soln}] / V[a]) / V[m(\text{std})])$$

Equation 6-2

Where:

$K[3] = 32.03 \text{ mg/meq. for metric units.}$

$= 7.061 \times 10^{-5} \text{ lb/meq. for English units.}$

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

$$RE = C[d] - C[a] / C[a] \times (100)$$

Eq. 6-3

Where:

$C[d] = \text{Determined audit sample concentration, mg/dscm.}$

$C[a] = \text{Actual audit sample concentration, mg/dscm.}$

SOURCE: [36 FR 24877, Dec. 23, 1971]

AUTHORITY: 42 U.S.C. 7401, 7411, 7414, 7416, and 7601.

Title 40 -- Protection of Environment; Revised as of July 1, 1991

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

§ 60. Appendix A to Part 60 -- Test Methods [PART III OF VII]

**40 CFR 60. Appendix A** to Part 60

### *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.

[SEE FIGURE IN ORIGINAL]

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

[SEE FIGURE IN ORIGINAL]

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.

Gauge/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 vacuum 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 an 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 (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:

$$V[\text{sb}(\text{std})] = V[\text{sb}] \times (T[\text{std}] / T[\text{amb}]) \times (P[\text{bar}] / P[\text{std}])$$

Eq. 6-4

$$Q[\text{std}] = V[\text{sb}(\text{std})] / \text{theta}$$

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, degrees K (degrees R).

T[std] = Standard absolute temperature, 273 degrees K (528 degrees R).

V[sb] = Volume of gas as measured by the soap bubble meter, m<sup>3</sup> (ft<sup>3</sup>).

V[sb(std)] = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).

THETA = Time, min.

[SEE FIGURE IN ORIGINAL]

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 percent, 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:

$$V[\text{m}(\text{std})] = Q[\text{std}] \text{ theta}[\text{s}] (1 - B[\text{wa}]) \times (P[\text{bar}] + P[\text{sr}] / P[\text{bar}] + P[\text{c}])$$

Eq. 6-6

where:

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

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

$B[\text{wa}]$  = Water vapor in ambient air, proportion by volume.

$\theta[\text{s}]$  = Sampling time, min.

$P[\text{c}]$  = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

$P[\text{sr}]$  = 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 saturated 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:

$$V[m](\text{std}) = Q[\text{std}] \theta[\text{s}] \times (1 - B[\text{wa}]) \times \sqrt{M[\text{a}] / M[\text{s}]} \times (P[\text{bar}] + P[\text{sr}] / P[\text{bar}] + P[\text{c}])$$

Eq. 6-7

where:

$M[\text{a}]$  = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

$M[\text{s}]$  = 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.

*7.3 Elimination of Ammonia Interference.* The following alternative procedures shall be used in addition to those specified in the method when sampling at sources having ammonia emissions.

*7.3.1 Sampling.* The probe shall be maintained at 275 degrees C and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO<sub>2</sub>. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Citation 10 of the Method 5 bibliography is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 degrees C.

*7.3.2 Sample Recovery.* Recover the sample according to Section 4.2 except for discarding the contents of the midjet bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to the polyethylene bottle containing the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midjet bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midjet bubbler to a separate polyethylene bottle.

*7.3.3 Sample Analysis.* Follow the procedures in Section 4.3, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer

flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated concentration will depend upon the ammonia to SO<sub>2</sub> ratio and the level of oxygen present in the gas stream. A fraction of the SO<sub>2</sub> will be counted as sulfur trioxide as the ammonia to SO<sub>2</sub> ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO<sub>2</sub> will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thiorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6-2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO<sub>2</sub> collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent hydrogen peroxide, 100 ml of 100 percent isopropanol, and two to four drops of thiorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V<sub>t</sub>, the volume of barium perchlorate used for the SO<sub>2</sub> sample.

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## METHOD 6A -- DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

### 1. *Principle and Applicability*

1.1 Applicability. This method applies to the determination of sulfur dioxide (SO<sub>2</sub>) emissions from fossil fuel combustion sources in terms of concentration (mg/m<sup>3</sup>) and in terms of emission rate (ng/J) and to the determination of carbon dioxide (CO<sub>2</sub>) concentration (percent). Moisture, if desired, may also be determined by this method.

The minimum detectable limit, the upper limit, and the interferences of the method for the measurement of SO<sub>2</sub> are the same as for Method 6. For a 20-liter sample, the method has a precision of 0.5 percent CO<sub>2</sub> for concentrations between 2.5 and 25 percent CO<sub>2</sub> and 1.0 percent moisture for moisture concentrations greater than 5 percent.

1.2 Principle. The principle of sample collection is the same as for Method 6 except that moisture and CO<sub>2</sub> are collected in addition to SO<sub>2</sub> in the same sampling train. Moisture and CO<sub>2</sub> fractions are determined gravimetrically.

### 2. *Apparatus*

2.1 Sampling. The sampling train is shown in Figure 6A-1; the equipment required is the same as for Method 6, Section 2.1, except as specified below:

2.1.1 SO<sub>2</sub> Absorbers. Two 30-ml midget impingers with a 1-mm restricted tip and two 30-ml midget bubblers with an unrestricted tip. Other types of impingers and bubblers, such as Mae West for SO<sub>2</sub> collection and rigid cylinders for moisture absorbers containing Drierite, may be used with proper attention to reagent volumes and levels, subject to the Administrator's approval.

2.1.2 CO<sub>2</sub> Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm and a length between 125 and 250 mm and with appropriate connections at both ends.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe inlet or any unheated section of the probe, such as the connection to the SO<sub>2</sub> absorber. The probe and filter should be heated to at least 20 deg. C above the source temperature, but not greater than 120 deg. C. The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: Mention of a brand name does not constitute endorsement by the Environmental Protection Agency.

2.2 Sample Recovery and Analysis. The equipment needed for sample recovery and analysis is the same as required for Method 6. In addition, a balance to measure within 0.05 g is needed for analysis.

### 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. The reagents required for sampling are the same as specified in Method 6. In addition, the following reagents are required:

Figure 6A-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

3.1.1 Drierite. Anhydrous calcium sulfate ( $\text{CaSO}_4$ ) desiccant, 8 mesh, indicating type is recommended. (Do not use silica gel or similar desiccant in the application.)

3.1.2  $\text{CO}_2$  Absorbing Material. Ascarite II. Sodium hydroxide coated silica, 8 to 20 mesh.

3.2 Sample Recovery and Analysis. The reagents needed for sample recovery and analysis are the same as for Method 6, Sections 3.2 and 3.3, respectively.

#### 4. Procedure

##### 4.1 Sampling.

4.1.1 Preparation of Collection Train. Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers as described in Method 6. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A-1. Into the fourth vessel in the train, the second midget bubbler, place about 25 g of Drierite. Clean the outsides of the bubblers and impingers, and weigh at room temperature (approx. = 20 degrees C) to the nearest 0.1 g. Weigh the four vessels simultaneously, and record this initial mass.

With one end of the  $\text{CO}_2$  absorber sealed, place glass wool in the cylinder to a depth of about 1 cm. Place about 150 g of  $\text{CO}_2$  absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in Figure 6A-2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The  $\text{CO}_2$  absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the  $\text{CO}_2$  absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and weigh at room temperature to the nearest 0.1 g. Record this initial mass.

Assemble the train as shown in Figure 6A-1. Adjust the probe heater to a temperature sufficient to prevent condensation (see Note in section 2.1.1). Place crushed ice and water around the impingers and bubblers. Mount the  $\text{CO}_2$  absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing, e.g., Tygon, may be used to connect the last  $\text{SO}_2$  absorbing bubbler to the Drierite absorber and to connect the Drierite absorber to the  $\text{CO}_2$  absorber. A second, smaller  $\text{CO}_2$  absorber containing Ascarite II may be added in line downstream of the primary  $\text{CO}_2$  absorber as a breakthrough indicator. Ascarite II turns white when  $\text{CO}_2$  is absorbed.

Figure 6A-2.  $\text{CO}_2$  absorber.

[SEE FIGURE IN ORIGINAL]

4.1.2 Leak-Check Procedure and Sample Collection. The leak-check procedure and sample collection procedure

are the same as specified in Method 6, Sections 4.1.2 and 4.1.3, respectively.

## 4.2. Sample Recovery.

4.2.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO<sub>2</sub> impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outsides of loose dirt and moisture, and weigh them simultaneously in the same manner as in Section 4.1.1. Record this final mass.

4.2.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with deionized distilled water, and add the washings to the same storage container.

4.2.3 CO<sub>2</sub> Absorber. Allow the CO<sub>2</sub> absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in Section 4.1.1. Record this final mass. Discard used Ascarite II material.

4.3 Sample Analysis. The sample analysis procedure for SO<sub>2</sub> is the same as specified in Method 6, Section 4.3.

4.4 Quality Assurance (QA) Audit Samples. Only when this method is used for compliance determinations, obtain an audit sample set as directed in Section 3.3.6 of Method 6. Analyze the audit samples, and report the results as directed in Section 4.4 of Method 6. Acceptance criteria for the audit results are the same as in Method 6.

## 5. Calibration

The calibrations and checks are the same as required in Method 6, Section 5.

## 6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations. The calculations, nomenclature, and procedures are the same as specified in Method 6 with the addition of the following:

6.1 Nomenclature.

C[w] = Concentration of moisture, percent.

C[CO<sub>2</sub>] = Concentration of CO<sub>2</sub>, dry basis, percent.

m[wi] = Initial mass of impingers, bubblers, and moisture absorber, g.

m[wf] = Final mass of impingers, bubblers, and moisture absorber, g.

m[ai] = Initial mass of CO<sub>2</sub> absorber, g.

m[af] = Final mass of CO<sub>2</sub> absorber, g.

V[CO<sub>2</sub>(std)] = Equivalent volume of CO<sub>2</sub> collected at standard conditions, dm<sup>3</sup>.

V[w(std)] = Equivalent volume of moisture collected at standard conditions, sm<sup>3</sup>.

$5.467 \times 10^{-4}$  = Equivalent volume of gaseous CO<sub>2</sub> at standard conditions per gram,  $\text{cm}^3/\text{g}$ .

$1.336 \times 10^{-3}$  = Equivalent volume of water vapor at standard conditions per gram,  $\text{cm}^3/\text{g}$ .

6.2 CO<sub>2</sub> Volume Collected, Corrected to Standard Conditions.

$$V[\text{CO}_2(\text{std})] = 5.467 \times 10^{-4}(m[\text{af}] - m[\text{ai}])$$

Eq. 6A-1

6.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V[\text{w}(\text{std})] = 1.336 \times 10^{-3}(m[\text{wf}] - m[\text{wi}])$$

Eq. 6A-2

6.4 SO<sub>2</sub> Concentration.

$$C[\text{SO}_2] = 32.03 (V[\text{t}] - V[\text{tb}])N (V[\text{soln}] V[\text{a}]) / V[\text{m}(\text{std})] + V[\text{CO}_2(\text{std})]$$

Eq. 6A-3

6.5 CO<sub>2</sub> Concentration.

$$C[\text{CO}_2] = V[\text{CO}_2(\text{std})] / V[\text{m}(\text{std})] + V[\text{CO}_2(\text{std})] \times 100$$

Eq. 6A-4

6.6 Moisture Concentration.

$$C[\text{w}] = V[\text{w}(\text{std})] / V[\text{m}(\text{std})] + V[\text{w}(\text{std})] + V[\text{CO}_2(\text{std})]$$

Eq. 6A-5

## 7. Emission Rate Procedure

If the only emission measurement desired is in terms of emission rate of SO<sub>2</sub> (ng/J), an abbreviated procedure may be used. The differences between Method 6A and the abbreviated procedure are described below.

7.1 Sample Train. The sample train is the same as shown in Figure 6A-1 and as described in Section 4, except that the dry gas meter is not needed.

7.2 Preparation of the Collection Train. Follow the same procedure as in Section 4.1.1, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers or the moisture absorber.

7.3 Sampling. Operate the train as described in Section 4.1.3, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded.

7.4 Sample Recovery. Follow the procedure in Section 4.2, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers, or the moisture absorber.

7.5 Sample Analysis. Analysis of the peroxide solution is the same as described in Section 4.3. Only when making compliance determinations, conduct an audit of the SO<sub>2</sub> analysis procedure as described in Section 4.4.

7.6 Calculations.

7.6.1 SO<sub>2</sub> Mass Collected.

$$m[\text{SO}_2] = 32.03 (V[t] - V[tb]) N (V[\text{soln}]/V[s])$$

Eq. 6A-7

Where:

$m[\text{SO}_2]$  = Mass of SO<sub>2</sub> collected, mg.

7.6.2 Sulfur Dioxide Emission Rate.

$$E[\text{SO}_2] = F[c] (1.829 \times 10^{-9}) m[\text{SO}_2] / (m[\text{af}] - m[\text{ai}])$$

Eq. 6A 8

Where:

$E[\text{SO}_2]$  = Emission rate of SO<sub>2</sub> (ng/J).

$F[c]$  = Carbon F Factor for the fuel burned, m<sup>3</sup>/J, from Method 19.

## 8. Bibliography

1. Same as for Method 6, Citations 1 through 8, with the addition of the following:
2. Stanley, Jon and P. R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. Vol. 3, No. 4. November 1978.
3. Whittle, Richard N. and P. R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO<sub>2</sub>/CO<sub>2</sub> Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pages.

## METHOD 6B -- DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

### 1. Principle and Applicability

1.1 Applicability. This method applies to the determination of sulfur dioxide (SO<sub>2</sub>) emissions from combustion sources in terms of concentration (ng/m<sup>3</sup>) and emission rate (ng/J), and for the determination of carbon dioxide (CO<sub>2</sub>) concentration (percent) on a daily (24 hours) basis.

The minimum detectable limits, upper limit, and the interferences for SO<sub>2</sub> measurements are the same as for Method 6. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the

studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (within laboratory precision) is 8.0 percent and the reproducibility (between laboratory precision) is 11.1 percent.

1.2 Principle. A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. Sampling may also be conducted continuously if the apparatus and procedures are appropriately modified (see Note in Section 4.1.1). The SO<sub>2</sub> and CO<sub>2</sub> are separated and collected in the sampling train. The SO<sub>2</sub> fraction is measured by the barium-thorin titration method, and CO<sub>2</sub> is determined gravimetrically.

## 2. Apparatus

The equipment required for this method is the same as specified for Method 6A, Section 2, except the isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets and does not allow direct contact between the collected liquid and the gas sample may be included in the train. For intermittent operation, include an industrial timer-switch designed to operate in the "on" position at least 2 minutes continuously and "off" the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. The probe and filter should be heated continuously to at least 20 deg. C above the source temperature, but not greater than 120 deg. C. The filter (i.e., sample gas) temperature should be monitored to assure the desired temperature is maintained.

Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential corrosion and contamination of sample. Glass probes or other types of stainless steel, e.g., Hasteloy or Carpenter 20, are recommended for long-term use.

Other sampling equipment, such as Mae West bubblers and rigid cylinders for moisture absorption, which requires sample or reagent volumes other than those specified in this procedure for full effectiveness may be used; subject to the approval of the Administrator.

## 3. Reagents

All reagents for sampling and analysis are the same as described in Method 6A, Section 3, except isopropanol is not used for sampling. The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Method 6. If Method 6B is to be operated in a low sample flow condition (less than 100 ml/min), molecular sieve material may be substituted for Ascarite II as the CO<sub>2</sub> absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5A deg., or equivalent. Molecular sieve material need not be discarded following the sampling run provided it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min may cause erroneous CO<sub>2</sub> results.

## 4. Procedure

### 4.1 Sampling.

4.1.1 Preparation of Collection Train. Preparation of the sample train is the same as described in Method 6A, Section 4.1.4, with the addition of the following:

The sampling train is assembled as shown in Figure 6A-1, except the isopropanol bubbler is not included. The

probe must be heated to a temperature sufficient to prevent water condensation and must include a filter (either in-stack, out-of-stack, or both) to prevent particulate entrainment in the peroxide impingers. The electric supply for the probe heat should be continuous and separate from the timed operation of the sample pump.

Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters for the amounts of sampling reagents prescribed in this method.

Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump (20 to 40 ml/min for the reagent volumes described in this method) is used. Then the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters for the amounts of sampling reagents prescribed in this method.

4.1.2 Leak-Check Procedure. The leak-check procedure is the same as described in Method 6, Section 4.1.2.

4.1.3 Sample Collection. Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Assure that the timer is operating as intended, i.e., in the "on" position for the desired period and the cycle repeats as required.

During the 24-hour sampling period, record the dry gas meter temperature one time between 9:00 a.m. and 11:00 a.m., and the barometric pressure.

At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak check as described in Section 4.1.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in this section (4.1.3) for successive runs.

4.2 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO<sub>2</sub> absorber) are the same as in Method 6A, Section 4.2.

4.3 Sample Analysis. Analysis of the peroxide impinger solutions is the same as in Method 6, Section 4.3.

4.4 Quality Assurance (QA) Audit Samples. Only when this method is used for compliance determinations, obtain an audit sample set as directed in Section 3.3.6 of Method 6. Analyze the audit samples at least once for every 30 days of sample collection, and report the results as directed in Section 4.4 of Method 6. The analyst performing the sample analyses shall perform the audit analyses. If more than one analyst performed the sample analyses during the 30-day sampling period, each analyses shall perform the audit analyses and all audit results shall be reported. Acceptance criteria for the audit results are the same as in Method 6.

## 5. Calibration

### 5.1 Metering System.

5.1.1 Initial Calibration. The initial calibration for the volume metering system is the same as for Method 6, Section 5.1.1.

5.1.2 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (1) The leak check is not to be conducted, (2) three or more revolutions of the dry gas meter must be used, and (3) 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 and use of the train can continue. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1; and for the calculations for the preceding 30 days of data, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run. Use the latest calibration factor for succeeding tests.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers initially and at 30-day intervals.

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

5.4 Barometer. Calibrate against a mercury barometer initially and at 30-day intervals.

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.

## 6. Calculations

The nomenclature and calculation procedures are the same as in Method 6A with the following exceptions:

P[bar] = Initial barometric pressure for the test period, mm Hg.

T[m] = Absolute meter temperature for the test period, deg. K.

## 7. Emission Rate Procedure

The emission rate procedure is the same as described in Method 6A, Section 7, except that the timer is needed and is operated as described in this method. Only when this method is used for compliance determinations, perform the QA audit analyses as described in Section 4.4.

## 8. Bibliography

The bibliography is the same as described in Method 6A, with the addition of the following:

1. Butler, Frank E; J. E. Knoll, J. C. Suggs, M. R. Midgett, and W. Mason. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO<sub>2</sub> and CO<sub>2</sub>. JAPCA. Vol. 33, No. 10. October 1983.

## METHOD 6C -- DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

### 1. Applicability and Principle

1.1 *Applicability*. This method is applicable to the determination of sulfur dioxide (SO<sub>2</sub>) concentrations in controlled and uncontrolled emissions from stationary sources only when specified within the regulations.

1.2 *Principle*. A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO<sub>2</sub> gas concentration using an ultraviolet (UV), nondispersive

infrared (NDIR), or fluorescence analyzer. Performance specifications and test procedures are provided to ensure reliable data.

## 2. *Range and Sensitivity*

2.1 Analytical Range. The analytical range is determined by the instrumental design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system. The span of the monitoring system shall be selected such that the pollutant gas concentration equivalent to the emission standard is not less than 30 percent of the span. If at any time during a run the measured gas concentration exceeds the span, the run shall be considered invalid.

2.2 Sensitivity. The minimum detectable limit depends on the analytical range, span, and signal-to-noise ratio of the measurement system. For a well designed system, the minimum detectable limit should be less than 2 percent of the span.

## 3. *Definitions*

3.1 Measurement System. The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzers from the effects of the stack effluent.

3.1.2 Gas Analyzer. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 Data Recorder. A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 Span. The upper limit of the gas concentration measurement range displayed on the data recorder.

3.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

3.4 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 Sampling System Bias. The difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and when the same gas is introduced directly to the analyzer.

3.6 Zero Drift. The difference in the measurement system output reading from the initial calibration response at the zero concentration level after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.7 Calibration Drift. The difference in the measurement system output reading from the initial calibration response at a mid-range calibration value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.8 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.9 Interference Check. A method for detecting analytical interferences and excessive biases through direct

comparison of gas concentrations provided by the measurement system and by a modified Method 6 procedure. For this check, the modified Method 6 samples are acquired at the sample by-pass discharge vent.

3.10 Calibration Curve. A graph or other systematic method of establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

#### 4. *Measurement System Performance Specifications*

4.1 Analyzer Calibration Error. Less than +/- 2 percent of the span for the zero, mid-range, and high-range calibration gases.

4.2 Sampling System Bias. Less than +/- 5 percent of the span for the zero, and mid- or high-range calibration gases.

4.3 Zero Drift. Less than +/- 3 percent of the span over the period of each run.

4.4 Calibration Drift. Less than +/- 3 percent of the span over the period of each run.

4.5 Interference Check. Less than +/- 7 percent of the modified Method 6 result for each run.

#### 5. *Apparatus and Reagents*

5.1 Measurement System. Any measurement system for SO<sub>2</sub> that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1. The essential components of the measurement system are described below:

5.1.1 Sample Probe. Glass, stainless steel, or equivalent, of sufficient length to traverse the sample points. The sampling probe shall be heated to prevent condensation.

5.1.2 Sample Line. Heated (sufficient to prevent condensation) stainless steel or Teflon tubing, to transport the sample gas to the moisture removal system.

5.1.3 Sample Transport Lines. Stainless steel or Teflon tubing, to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

5.1.4 Calibration Valve Assembly. A three-way valve assembly, or equivalent, for blocking the sample gas flow and introducing calibration gases to the measurement system at the outlet of the sampling probe when in the calibration mode.

5.1.5 Moisture Removal System. A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas. The moisture removal system is not necessary for analyzers that can measure gas concentrations on a wet basis; for these analyzers, (1) heat the sample line and all interface components up to the inlet of the analyzer sufficiently to prevent condensation, and (2) determine the moisture content and correct the measured gas concentrations to a dry basis using appropriate methods, subject to the approval of the Administrator. The determination of sample moisture content is not necessary for pollutant analyzers that measure concentrations on a wet basis when (1) a wet basis CO<sub>2</sub> analyzer operated according to Method 3A is used to obtain simultaneous measurements, and (2) the pollutant/CO<sub>2</sub> measurements are used to determine emissions in units of the standard.

5.1.6 Particulate Filter. An in-stack or heated (sufficient to prevent water condensation) out-of-stack filter. The filter shall be borosilicate or quartz glass wool, or glass fiber mat. Additional filters at the inlet or outlet of the

moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of the components. All filters shall be fabricated of materials that are nonreactive to the gas being sampled.

5.1.7 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is nonreactive to the gas being sampled.

5.1.8 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent.

(NOTE: The tester may elect to install a back-pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzer(s) from overpressurization, and to minimize the need for flow rate adjustments.)

5.1.9 Sample Gas Manifold. A sample gas manifold, to divert a portion of the sample gas stream to the analyzer, and the remainder to the by-pass discharge vent. The sample gas manifold should also include provisions for introducing calibration gases directly to the analyzer. The manifold may be constructed of any material that is nonreactive to the gas being sampled.

5.1.10 Gas Analyzer. A UV or NDIR absorption or fluorescence analyzer, to determine continuously the SO<sub>2</sub> concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer.

(NOTE: Housing the analyzer(s) in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.)

5.1.11 Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be obtained.

5.2 Method 6 Apparatus and Reagents. The apparatus and reagents described in Method 6, and shown by the schematic of the sampling train in Figure 6C-2, to conduct the interference check.

5.3 SO<sub>2</sub> Calibration Gases. The calibration gases for the gas analyzer shall be SO<sub>2</sub> in N<sub>2</sub> or SO<sub>2</sub> in air. Alternatively, SO<sub>2</sub>/CO<sub>2</sub>, SO<sub>2</sub>/O<sub>2</sub>, or SO<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> gas mixtures in N<sub>2</sub> may be used. For fluorescence-based analyzers, the O<sub>2</sub> and CO<sub>2</sub> concentrations of the calibration gases as introduced to the analyzer shall be within 1 percent (absolute) CO<sub>2</sub> of the O<sub>2</sub> and CO<sub>2</sub> concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO<sub>2</sub> in air and the nomographs provided by the vendor to determine the quenching correction factor (the effluent O<sub>2</sub> and CO<sub>2</sub> concentrations must be known). Use three calibration gases as specified below:

5.3.1 High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

5.3.2 Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

5.3.3 Zero Gas. Concentration of less than 0.25 percent of the span. Purified ambient air may be used for the zero gas by passing air through a charcoal filter, or through one or more impingers containing a solution of 3 percent H<sub>2</sub>O<sub>2</sub>.

## 6. Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Gas Concentration Verification. There are two alternatives for establishing the concentrations of calibration gases. Alternative Number 1 is preferred.

6.1.1 Alternative Number 1--Use of calibration gases that are analyzed following the Environmental Protection Agency Traceability Protocol Number 1 (see Citation 1 in the Bibliography). Obtain a certification from the gas manufacturer that Protocol Number 1 was followed.

6.1.2 Alternative Number 2--Use of calibration gases not prepared according to Protocol Number 1. If this alternative is chosen, obtain gas mixtures with a manufacturer's tolerance not to exceed  $\pm 2$  percent of the tag value. Within 6 months before the emission test, analyze each of the calibration gases in triplicate using Method 6. Citation 2 in the Bibliography describes procedures and techniques that may be used for this analysis. Record the results on a data sheet (example is shown in Figure 6C-3). Each of the individual SO<sub>2</sub> analytical results for each calibration gas shall be within 5 percent (or 5 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set, and repeat the triplicate analyses. If the average of the triplicate analyses is within 5 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree with 5 percent (or 5 ppm, whichever is greater) of their average. Then use this average for the cylinder value.

6.2 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve correct sampling rates.

6.3 Analyzer Calibration Error. Conduct the analyzer calibration error check by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

6.3.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas on a form similar to Figure 6C-4.

NOTE: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

6.3.2 The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds  $\pm 2$  percent of the span for any of the calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the analyzer calibration error check until acceptable performance is achieved.

6.4 Sampling System Bias Check. Perform the sampling system bias check by introducing calibration gases at the calibration valve installed at the outlet of the sampling probe. A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, shall be used for this check as follows:

6.4.1 Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer on a form similar to Figure 6C-5. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times as the response time.

6.4.2 The sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the analyzer calibration error check and for the sampling system bias check exceeds +/-5 percent of the span for either the zero or upscale calibration gas. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

## *7. Emission Test Procedure*

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 6.

7.2 Interference Check Preparation. For each individual analyzer, conduct an interference check for at least three runs during the initial field test on a particular source category. Retain the results, and report them with each test performed on that source category.

If an interference check is being performed, assemble the modified Method 6 train (flow control valve, two midjet impingers containing 3 percent H<sub>2</sub>O and dry gas meter) as shown in Figure 6C-2. Install the sampling train to obtain a sample at the measurement system sample by-pass discharge vent. Record the initial dry gas meter reading.

7.3 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., +/-10 percent) during the entire run. The sampling time per run shall be the same as for Method 6 plus twice the system response time. For each run, use only those measurements obtained after twice response time of the measurement system has elapsed, to determine the average effluent concentration. If an interference check is being performed, open the flow control valve on the modified Method 6 train concurrent with the initiation of the sampling period, and adjust the flow to 1 liter per minute (+/-10 percent).

(NOTE: If a pump is not used in the modified Method 6 train, caution should be exercised in adjusting the flow rate since overpressurization of the impingers may cause leakage in the impinger train, resulting in positively biased results).

7.4 Zero and Calibration Drift Tests. Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in Section 6.4 (Make no adjustments to the measurement system until after the drift checks are completed.) Record and analyzer's responses on a form similar to Figure 6C-5.

7.4.1 If either the zero or upscale calibration value exceeds the sampling system bias specification, then the run is considered invalid. Repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before repeating the run.

7.4.2 If both the zero and upscale calibration values are within the sampling system bias specification, then use

the average of the initial and final bias check values to calculate the gas concentration for the run. If the zero or upscale calibration drift value exceeds the drift limits, based on the difference between the sampling system bias check responses immediately before and after the run, repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before conducting additional runs.

7.5 Interference Check (if performed). After completing the run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers, and determine the SO<sub>2</sub> gas concentration using the procedures of Method 6. (It is not necessary to analyze EPA performance audit samples for Method 6.) Determine the average gas concentration exhibited by the analyzer for the run. If the gas concentrations provided by the analyzer and the modified Method 6 differ by more than 7 percent of the modified Method 6 result, the run is invalidated.

## 8. Emission Calculation

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer, and is adjusted for the zero and upscale sampling system bias checks, as determined in accordance with Section 7.4. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be used. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be used. Calculate the effluent gas concentration using Equation 6C-1.

$$C[\text{gas}] = (C - C[o]) \times C[\text{ma}] / C[\text{m}] - C[o]$$

Eq. 6C-1

Where:

C[*gas*] = Effluent gas concentration, dry basis, ppm.

C = Average gas concentration indicated by gas analyzer, dry basis, ppm.

C[*o*] = Average of initial and final system calibration bias check responses for the zero gas, ppm.

C[*m*] = Average of initial and final system calibration bias check responses for the upscale calibration gas, ppm.

C[*ma*] = Actual concentration of the upscale calibration gas, ppm.

## 9. Bibliography

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[SEE FIGURE IN ORIGINAL]

FIGURE 6C-3--ANALYSIS OF CALIBRATION GASES

Date Analytic method used

**Gas concentration**  
**(indicate units)**

	<b>Mid-</b>	<b>High-</b>
<b>Zero</b>		
<b>na</b>		
	<b>range</b>	<b>range</b>
	<b>nb</b>	<b>nc</b>

Sample run:

- 1
- 2
- 3

Average

Maximum percent deviation

na Average must be less than 0.25 percent of span.

nb Average must be 50 to 60 percent of span.

nc Average must be 80 to 90 percent of span.

#### FIGURE 6C-4--ANALYZER CALIBRATION DATA

Source Analyzer calibration data for  
identification: sampling  
Test personnel: runs:  
Date: Span:

<b>Analyzer</b>			
<b>Cylinder calibration</b>	<b>Absolute</b>		
<b>value</b>	<b>response</b>	<b>Differenc</b>	
<b>(indicate</b>	<b>(indicate</b>	<b>e</b>	<b>(percent</b>
<b>units)</b>	<b>units)</b>	<b>units)</b>	<b>of span)</b>

Zero gas  
Mid-range gas  
High-range gas

#### FIGURE 6C-5--SYSTEM CALIBRATION BIAS AND DRIFT DATA

Source identification: Run number:  
 Test personnel: Span:  
 Date:

Analyzer	System	Initial values		Final values	
		cal. bias	System calibration (percent of span)	cal. bias	System calibration (percent of span)
calibration	calibration	(percent response)	(percent response)	(percent response)	(percent response)
	response	response	of span)	response	of span)

Zero gas  
 Upscale gas

$$\text{System Calibration Bias} = \frac{\text{System Cal. Response} - \text{Analyzer Cal. Response}}{\text{Span}} \times 100$$

$$\text{Drift} = \frac{\text{Final System Cal. Response} - \text{Initial System Cal. Response}}{\text{Span}} \times 100$$

## 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 n3 tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

n3 Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

[SEE FIGURE IN ORIGINAL]

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 deg. C (2 deg. F) intervals from -5 to 50 deg. C (25 to 125 deg. 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.

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 deg. C (160 deg. 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  $\text{KNO}_3$  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  $\text{H}_2\text{SO}_4$  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(1N). 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  $\text{KMnO}_4$  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 deg. C (220 to 230 deg. F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.5 Standard  $\text{KNO}_3$  Solution. Dissolve exactly 2.198 g of dried potassium nitrate ( $\text{KNO}_3$ ) 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  $\text{KNO}_3$  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  $\mu\text{g}$  nitrogen dioxide ( $\text{NO}_2$ ).

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 deg. C (212 deg. 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 enforcement 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 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 ( $T_f$ ), 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 ( $P_f$ ) 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  $\text{NO}$  to  $\text{NO}_2$  (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of  $\text{NO}$  in  $\text{N}_2$ ), 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 porcelain 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  $\mu\text{g NO}_2$  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  $\mu\text{g NO}_2$  / 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 spectrophotometer 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  $\mu\text{g}$   $\text{NO}_2$  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  $\text{KNO}_3$  working standard solution (1 ml = 100  $\mu\text{g}$   $\text{NO}_2$ ) 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:

$$K[c] = 100 \times A[1] + 2A[2] + 3A[3] + 4A[4] / A[1]^{<2>} + A[2]^{<2>} + A[3]^{<2>} + A[4]^{<2>}$$

Eq. 7-1

Where:

K[c] = Calibration factor,  $\mu\text{g}$ .

A[1] = Absorbance of the 100 -  $\mu\text{g}$  NO<sub>2</sub> standard.

A[2] = Absorbance of the 200 -  $\mu\text{g}$  NO<sub>2</sub> standard.

A[3] = Absorbance of the 300 -  $\mu\text{g}$  NO<sub>2</sub> standard.

A[4] = Absorbance of the 400 -  $\mu\text{g}$  NO<sub>2</sub> 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  $\mu\text{g}$  NO<sub>2</sub>) 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<sub>x</sub> as NO<sub>2</sub>, 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<sub>x</sub> as NO<sub>2</sub> in gas sample,  $\mu\text{g}$ .

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, deg. K ( deg. R).

T[i] = Initial absolute temperature of flask, deg. K ( deg. R).

T[std] = Standard absolute temperature 293 deg. K (528 deg. R).

V[sc] = Sample volume at standard conditions (dry basis), ml.

V[f] = Volume of flask and valve, ml.

V[a] = Volume of absorbing solution, 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.

$$V[sc] = (T[std]/P[std])(V[f] - V[a])(P[f]/T[f] - P[i]/T[i])$$
$$= K[1] (V[f] - 25 \text{ ml})(P[f]/T[f] - P[i]/T[i])$$

Eq. 7-2

Where:

K[1] = 0.3858 deg. K / mm Hg for metric units

= 17.64 deg. R / in. Hg for English units.

#### 6.3 Total $\mu\text{g NO}_2$ Per Sample.

$$m = 2K[c]A F$$

Eq. 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.

$$C = K[2] X m / V[sc]$$

Equation 7-4

Where:

K[2] =  $10^3$  (mg/scm) /  $\mu\text{g/ml}$  for metric units.

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

To convert from mg/dscm to g/dscm, divide C by 1,000.

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

$$RE = \frac{C[d] - C[a]}{C[a]} \times 100$$

Eq. 7-5

Where:

C[d] = Determined audit sample concentration, mg/dscm.

C[a] = Actual audit sample concentration, mg/dscm.

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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<sub>x</sub> / m<sup>3</sup> as NO<sub>2</sub> (65 to 655 ppm), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m<sup>3</sup> (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, CA. 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 ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is required for sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated  $\text{H}_2\text{SO}_4$  to a 1-liter flask containing water (same as Section 3.2). Add 6 ml of 3 percent  $\text{H}_2\text{O}_2$  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  $\text{KMnO}_4$

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<sub>2</sub>/ml. Dry an adequate amount of sodium nitrate (NaNO<sub>3</sub>) at 105 to 110 deg. C for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried NaNO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub>) and 1.008 g of sodium bicarbonate (NaHCO<sub>3</sub>), and dissolve in 4 liters of water. This solution is 0.0024 M Na<sub>2</sub>CO<sub>3</sub>/0.003 M NaHCO<sub>3</sub>. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

3.3.5 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 analysis 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  $\mu$ g/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250  $\mu$ g.) 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  $\mu$ g (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  $\mu$ g).

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:

$$C = \text{HSF} \times 10^{<4>} / V[\text{sc}]$$

Eq. 7A-1

Where:

H = Sample peak height, mm.

S = Calibration factor,  $\mu$ g/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

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

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

If desired, the concentration of NO<sub>2</sub> may be calculated as ppm NO<sub>2</sub> at standard conditions as follows:

$$\text{ppm NO}_2 = 0.5228 C$$

Eq. 7A-2

Where:

$$0.5228 = \text{ml/mg NO}_2.$$

## 7. Bibliography

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## METHOD 7B -- DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRY)

### 1. Applicability and Principle

1.1 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from nitric acid plants. The range of the method as outlined has been determined to be 57 to 1,500 milligrams NO<sub>x</sub> (as NO<sub>2</sub>) per dry standard cubic meter, or 30 to 786 ppm NO<sub>x</sub> (as NO<sub>2</sub>), assuming corresponding standards are prepared.

1.2 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 by ultraviolet absorption.

### 2. Apparatus

2.1 Sampling. Same as Method 7, Section 2.1.1 through Section 2.1.11.

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

2.2.1 Wash Bottle. Polyethylene or glass.

2.2.2 Volumetric Flasks. 100-ml (one for each sample).

2.3 Analysis. The following equipment is needed for analysis:

2.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20- ml to make standards and sample dilutions.

2.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

2.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

2.3.4 Analytical Balance. To measure to within 0.1 mg.

### 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. Same as Method 7, Section 3.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

3.2 Sample Recovery. Same as for Method 7, Section 3.2.2.

3.3 Analysis. Same as for Method 7, Sections 3.3.4, 3.3.5, and 3.3.7 with the addition of the following:

3.3.1 Working Standard KNO<sub>3</sub> Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 µg nitrogen dioxide (NO<sub>2</sub>).

3.3.2 Absorbing Solution. Same as in Section 3.1.

3.3.3 Quality Assurance Audit Samples. Nitrate samples are prepared in glass vials by the Environmental Protection Agency (EPA), Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina. Each set will consist of two vials with two unknown concentrations. When making compliance determinations, obtain the audit samples from the quality assurance management office at each EPA regional office.

### 4. *Procedures*

4.1 Sampling. Same as Method 7, Sections 4.1.1 and 4.1.2.

4.2 Sample Recovery. Let the flask sit 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<sub>f</sub>), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P<sub>f</sub>) is the barometric pressure less the manometer reading.

Transfer the contents of the flask to a 100-ml volumetric flask. Rinse the flask three times with 10-ml portions of water, and add to the volumetric flask. Dilute to 100 ml with water. Mix thoroughly. The sample is now ready for analysis.

4.3 Analysis. Pipette a 20-ml aliquot of sample into a 100-ml volumetric flask. Dilute to 100 ml with water. The

sample is now ready to be read by ultraviolet spectrophotometry. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

4.4 Audit Analysis. With each set of compliance samples or once per analysis day, or once per week when averaging continuous samples, analyze each performance audit in the same manner as the sample to evaluate the analyst's technique and standard preparation. The same person, the same reagents, and the same analytical system must be used both for compliance determination samples and the EPA audit samples. Report the results of all audit samples with the results of the compliance determination samples. The relative error will be determined by the regional office or the appropriate enforcement agency.

## 5. Calibration

Same as Method 7, Section 5.1 and Sections 5.3 through 5.6 with the addition of the following:

5.1 Determination of Spectrophotometer Standard Curve. Add 0.0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO<sub>3</sub> working standard solution (1 ml = 10 µg NO<sub>2</sub>) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO<sub>2</sub>, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO<sub>2</sub>.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used. Calculate the spectrophotometer calibration factor K<sub>c</sub> as follows:

$$K[c] = \frac{\sum_{i=1}^n M[i] A[i]}{\sum_{i=1}^n A[i]}$$

Eq. 7B-1

Where:

m[i] = Mass of NO<sub>2</sub> in standard i, µg.

A[i] = Absorbance of NO<sub>2</sub> standard i.

N = Total number of calibration standards.

For the set of calibration standards specified here, Equation 7-1 simplifies to the following:

$$K[c] = \frac{50 A[1] + 2A[2] + 3A[3] + 4A[4]}{A[1] + A[2] + A[3] + A[4]}$$

Eq. 7B-2

## 6. Calculations

Same as Method 7, Sections 6.1, 6.2, and 6.4 with the addition of the following:

6.1 Total µg NO<sub>2</sub> Per Sample:

$$m = 5K[c]AF$$

Eq. 7B-3

Where:

$5 = 100/20$ , the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

## 6.2 Relative Error (RE) for Quality Assurance Audits.

$$RE = \frac{C[d] - C[a]}{C[a]} \times 100$$

Eq. 7B-4

Where:

C[d] = Determined audit concentration.

C[a] = Actual audit concentration.

## 7. Bibliography

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2. Rennie, P. J., A. M. Sumner, and F. B. Basketter. "Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry." "Analyst." Vol. 104. September 1979. p. 837.

## METHOD 7C -- DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES -- ALKALINE-PERMANGANATE/COLORIMETRIC METHOD

### 1. *Applicability, Principle, Interferences, Precision, Bias, and Stability*

1.1 Applicability. The method is applicable to the determination of NO[x] emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations. The lower detectable limit is 13 mg NO[x]/m<sup>3</sup>, as NO<sub>2</sub> (7 ppm NO[x]) when sampling at 500 cc/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO[x] emissions quantitatively up to 1,782 mg NO[x]/m<sup>3</sup>, as NO<sub>2</sub> (932 ppm NO[x]).

1.2 Principle. An integrated gas sample is extracted from the stack and collected in alkaline-potassium permanganate solution; NO[x] (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>2</sub> and NO<sub>3</sub>. The NO<sub>3</sub> is reduced to NO<sub>2</sub> with cadmium, and the NO<sub>2</sub> is analyzed colorimetrically.

1.3 Interferences. Possible interferences are SO<sub>2</sub> and NH<sub>3</sub>. High concentrations of SO<sub>2</sub> could interfere because SO<sub>2</sub> consumes MnO<sub>4</sub> (as does NO[x]) and, therefore, could reduce the NO[x] collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1-percent sulfur coal with no control of SO<sub>2</sub> emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO<sub>2</sub> will reduce the MnO<sub>4</sub> concentration by only 5 percent if all the SO<sub>2</sub> is consumed in the first impinger.

NH<sub>3</sub> is slowly oxidized to NO<sub>3</sub> by the absorbing solution. At 100 ppm NH<sub>3</sub> in the gas stream, an

interference of 6 ppm NO<sub>x</sub> (11 mg NO<sub>2</sub>/m<sup>3</sup>) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH<sub>3</sub> injection to control NO<sub>x</sub> emissions unless means are taken to correct the results. An equation has been developed to allow quantitation of the interference and is discussed in Citation 5 of the Bibliography.

1.4 Precision and Bias. The method does not exhibit any bias relative to Method 7. The within-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO<sub>x</sub>, respectively.

1.5 Stability. Collected samples are stable for at least 4 weeks.

## 2. Apparatus

2.1 Sampling and Sample Recovery. The sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated.

[SEE FIGURE IN ORIGINAL]

Figure 7C-1. NO<sub>x</sub> sampling train.

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 tubing may also be used for the probe. (Note: Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.)

2.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower until they become available commercially.)

[SEE FIGURE IN ORIGINAL]

Figure 7C-2. Restricted orifice impinger.

2.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, Sections 2.1.3, 2.1.4, 2.1.6, 2.1.7, 2.1.8, 2.1.11, and 2.1.12, respectively.

2.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate between 400 and 500 cc/min. For rotameters, a range of 0 to 1 liter/min is recommended.

2.1.5 Volume Meter. Dry gas meter capable of measuring the sample volume, under the sampling conditions of 400 to 500 cc/min for 60 minutes within an accuracy of 2 percent.

2.1.6 Filter. To remove NO<sub>x</sub> from ambient air, prepared by adding 20 g of a 5-angstrom molecular sieve to a cylindrical tube, e.g., a polyethylene drying tube.

2.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

2.1.8 Funnel and Stirring Rods. For sample recovery.

2.2 Sample Preparation and Analysis.

- 2.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.
- 2.2.2 Beakers. 400-, 600-, and 1000-ml capacities.
- 2.2.3 Filtering Flask. 500-ml capacity with side arm.
- 2.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.
- 2.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.
- 2.2.6 Stirring Rods.
- 2.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.
- 2.2.8 Watch Glasses. To cover 600- and 1,000-ml beakers.
- 2.2.9 Graduated Cylinders. 50- and 250-ml capacities.
- 2.2.10 Pipettes. Class A
- 2.2.11 pH Meter. To measure pH from 0.5 to 12.0
- 2.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalogue No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm from the top of plug, and have a glass blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.
- 2.2.13 Glass Funnel. 75-mm ID at the top.
- 2.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm. One-cm cells are adequate.
- 2.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 deg. C.
- 2.2.16 Culture Tubes. 20- by 150-mm, Kimax No. 45048.
- 2.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.
- 2.2.18 CO<sub>2</sub> Measurement Equipment. Same as in Method 3.

### 3. *Reagents*

Unless otherwise indicated, all reagents should 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 Water. Deionized distilled to conform to ASTM Specification D 1193-74, Type 3 (incorporated by reference -- see § 60.17).

3.1.2 Potassium Permanganate, 4.0 percent (w/w), Sodium Hydroxide, 2.0 percent (w/w). Dissolve 40.0 g of  $\text{KMnO}_4$  and 20.0 g of NaOH in 940 ml of water.

### 3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Sulfuric Acid. Concentrated  $\text{H}_2\text{SO}_4$ .

3.2.3 Oxalic Acid Solution. Dissolve 48 g of oxalic acid  $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$  in water, and dilute to 500 ml. Do not heat the solution.

3.2.4 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

3.2.5 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water and dilute to 100 ml.

3.2.6 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 Percent. Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Solution is best accomplished by using a magnetic stirrer.

3.2.7 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to 11.7 to 12.0 with 0.5 N NaOH.

3.2.8 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500-ml volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

3.2.9 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 deg. C) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

3.2.10 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA, showing more than one absorption peak over this range, is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

3.2.11 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalogue No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION:  $\text{H}_2$  is liberated during preparation. Prepare in an exhaust hood away from any flame.

3.2.12  $\text{NaNO}_2$  Standard Solution, Nominal Concentration, 1000  $\mu\text{g NO}_2/\text{ml}$ . Desiccate  $\text{NaNO}_2$  overnight. Accurately weigh 1.4 to 1.6 g of  $\text{NaNO}_2$  (assay of 97 percent  $\text{NaNO}_2$  or greater), dissolve in water, and dilute to 1 liter. Calculate the exact  $\text{NO}_2$  concentration from the following relationship:

$$\mu\text{g NO}_2/\text{ml} = \text{g of NaNO}_2 \times \text{purity, \%} / 100 \times 10^3 \times 46.01 / 69.01$$

This solution is stable for at least 6 months under laboratory conditions.

3.2.13  $\text{KNO}_3$  Standard Solution. Dry  $\text{KNO}_3$  at 110 deg. C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of  $\text{KNO}_3$  to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact  $\text{NO}_3$  concentration from the following relationship:

$\mu\text{g NO}_3^-/\text{ml} = \text{g of KNO}_3 \times 10^{-3} \times 62.01 / 101.10$

This solution is stable for 2 months without preservative under laboratory conditions.

3.2.14 Spiking Solution. Pipette 7 ml of the  $\text{KNO}_3$  standard into a 100-ml volumetric flask, and dilute to volume.

3.2.15 Blank Solution. Dissolve 2.4 g of  $\text{KMnO}_4$  and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of  $\text{KMnO}_4/\text{NaOH}$  solution to 100 ml.

3.2.16 Quality Assurance Audit Samples. Same as in Method 7, Section 3.3.9. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7C.

#### 4. Procedure

##### 4.1 Sampling.

4.1.1 Preparation of Collection Train. Add 200 ml of  $\text{KMnO}_4/\text{NaOH}$  solution (3.1.2) to each of three impingers, and assemble the train as shown in Figure 7C-1. Adjust probe heater to a temperature sufficient to prevent water condensation.

4.1.2 Leak-Check Procedure. A leak-check prior to the sampling run should be carried out; a leak-check after the sampling run is mandatory. Carry out the leak-check(s) according to Method 6, Section 4.1.2.

4.1.3 Check of Rotameter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter (2.1.6). Start the pump, and adjust the rotameter to read between 400 and 500 cc/min. After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter (DGM), and the sampling time. Collect enough volume to measure accurately the flow rate, and calculate the flow rate. This average flow rate must be less than 500 cc/min for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

4.1.4 Sample Collection. Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations, e.g., § 60.46(c) of 40 CFR Part 60. Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 cc/min. **CAUTION: HIGHER FLOW RATES WILL PRODUCE LOW RESULTS.** Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point. [NOTE. -- When the  $\text{SO}_2$  concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with  $\text{MnO}_2$ . For RA tests with  $\text{SO}_2$  greater than 1200 ppm, sample for 30 minutes (10 minutes at each point)]. Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct a leak-check as in Section 4.1.2. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

4.1.5  $\text{CO}_2$  Measurement. During sampling, measure the  $\text{CO}_2$  content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times -- near the start, midway, and before the end of a run and the average  $\text{CO}_2$  concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

4.2 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer

by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

4.3 Sample Preparation for Analysis. Prepare a cadmium reduction column as follows: Fill the burette (2.2.12) with water. Add freshly prepared cadmium slowly with tapping until no further settling occurs. The height of the cadmium column should be 39 cm. When not in use, store the column under rinse solution (3.2.7). (NOTE. -- The column should not contain any bands of cadmium fines. This may occur if regenerated column is used and will greatly reduce the column lifetime.)

Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

Take a 100-ml aliquot of the sample and blank (unexposed  $\text{KMnO}_4/\text{NaOH}$ ) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated  $\text{H}_2\text{SO}_4$  with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 deg. C. Keep the temperature below 60 deg. C. Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the  $\text{KMnO}_4$  solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated  $\text{H}_2\text{SO}_4$  until a clear solution is obtained.

Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to 11.7 to 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (250-ml may be required), and dilute to volume. The samples are now ready for  $\text{NO}_2$  analysis. [NOTE. -- Both the sample and blank should go through this procedure. Additionally, two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest  $\text{NO}_3$  concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see 6.2.1) is below 95 percent, prepare a new column, and repeat the cadmium reduction].

4.4 Sample Analysis. Pipette 10 ml of sample into a culture tube. (NOTE. -- Some test tubes give a high blank  $\text{NO}_2$  value but culture tubes do not.) Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed  $\text{KMnO}_4/\text{NaOH}$  solution (3.1.2). Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the

absorbance at 540 nm against water. Read  $\mu\text{g NO}_2/\text{ml}$  from the calibration curve. If the absorbance is greater than that of the highest calibration standard, pipette less than 10 ml of sample and enough water to make the total sample volume 10 ml, and repeat the analysis. Determine the  $\text{NO}_2$  concentration using the calibration curve obtained in Section 5.3.

4.5 Audit Analysis. This is the same as in Method 7, Section 4.4.

## 5. Calibration

### 5.1 Dry Gas Metering System (DGM).

5.1.1 Initial Calibration. Same as in Method 6, Section 5.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 4 in the Bibliography be consulted.

5.1.2 Post-Test Calibration Check. Same as in Method 6, Section 5.1.2.

5.2 Thermometers for DGM and Barometer. Same as in Method 6, Sections 5.2 and 5.4, respectively.

5.3 Calibration Curve for Spectrophotometer. Dilute 5.0 ml of the  $\text{NaNO}_2$  standard solution to 200 ml with water. This solution nominally contains  $25 \mu\text{g NO}_2/\text{ml}$ . Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00  $\mu\text{g NO}_2/\text{ml}$ . Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

Run standards and a water blank as instructed in Section 4.4. Plot the net absorbance vs  $\mu\text{gNO}_2/\text{ml}$ . Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/ $\mu\text{g NO}_2/\text{ml}$ . The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

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

$$V[\text{m}(\text{std})] = V[\text{m}]XY X T[\text{std}] T[\text{m}] X P[\text{bar}] / P[\text{std}] = K[1]XY X V[\text{m}]P[\text{bar}] / T[\text{m}] \text{ Eq. 7C-1}$$

Where:

$V[\text{m}(\text{std})]$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

$V[\text{m}]$  = Dry gas volume as measured by the dry gas meter, dcm.

$Y$  = Dry gas meter calibration factor.

$X$  = Correction factor for  $\text{CO}_2$  collection.

$$= 100 / 100 - \% \text{CO}_2(v / v)$$

$P[\text{bar}]$  = Barometric pressure, mm Hg.

$P[\text{std}]$  = Standard absolute pressure, 760 mm Hg.

T[m] = Average dry gas meter absolute temperature, deg. K.

T[std] = Standard absolute temperature, 293 deg. K.

K[1] = 0.3858 deg. K/mm Hg.

6.2 Total  $\mu\text{g NO}_2$  Per Sample.

6.2.1 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = (x - y) 200 / S \times 1.0 \times 46.01 / 62.01 = 269.6 (x - y) / s \text{ (Eq. 7C-2)}$$

Where:

E = Column efficiency, unitless.

x = Analysis of spiked sample,  $\mu\text{g NO}_2/\text{ml}$ .

y = Analysis of unspiked sample,  $\mu\text{g NO}_2/\text{ml}$ .

200 = Final volume of sample and blank after passing through the column, ml

s = Concentration of spiking solution,  $\mu\text{g NO}_3^-/\text{ml}$ .

1.0 = Volume of spiking solution added, ml.

46.01 =  $\mu\text{g NO}_2/\mu\text{mole}$ .

62.01 =  $\mu\text{g NO}_3^-/\mu\text{mole}$ .

6.2.2 Total  $\mu\text{g NO}_2$ .

$$m = (S-B) / E \times 200 \times 500 / 50 \times 1000 / 100 = (2 \times 10^4) (S-B) / E \text{ Eq. 7C-3}$$

Where:

m = Mass of  $\text{NO}_x$ , as  $\text{NO}_2$ , in sample,  $\mu\text{g}$ .

S = Analysis of sample,  $\mu\text{gNO}_2/\text{ml}$ .

B = Analysis of blank,  $\mu\text{gNO}_2/\text{ml}$ .

500 = Total volume of prepared sample, ml.

50 = Aliquot of prepared sample processed through cadmium column, ml.

100 = Aliquot of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

1000 = Total volume of  $\text{KMnO}_4/\text{NaOH}$  solution ml.

6.3 Sample Concentration.

$$C = K[2] m / V[m(std)]$$

Where:

C = Concentration of NO[x] as NO[2], dry basis, mg/dscm.

$$K[2] = 10^{-3} \text{ mg}/\mu\text{g}$$

#### 6.4 Conversion Factors.

$$1.0 \text{ ppm NO} = 1.247 \text{ mg NO}/\text{m}^3 \text{ at STP.}$$

$$1.0 \text{ ppm NO}_2 = 1.912 \text{ mg NO}_2/\text{m}^3 \text{ at STP.}$$

$$1 \text{ ft}^3 = 2.832 \times 10^{-2} \text{ m}^3.$$

$$1000 \text{ mg} = 1 \text{ g.}$$

#### 7. *Quality Control*

Quality control procedures are specified in Sections 4.1.3 (flow rate accuracy); 4.3 (cadmium column efficiency); 4.4 (calibration curve accuracy); and 4.5 (audit analysis accuracy).

#### 8. *Bibliography*

1. Margeson, J. H., W. J. Mitchell, J. C. Suggs, and M. R. Midgett. Integrated Sampling and Analysis Methods for Determining NO[x] Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. 32:1210-1215.1982.
2. Memorandum and attachment from J. H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH[3] Interference in Methods 7C and 7D.
3. Margeson, J. H., J. C. Suggs, and M. R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. 52:1955-57. 1980.
4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III -- Stationary Source Specific Methods. August 1977. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-77-027b. August 1977.
5. Margeson, J. H., et al. An Integrated Method for Determining NO[x] Emissions at Nitric Acid Plants. Manuscript submitted to Analytical Chemistry. April 1984.

#### METHOD 7D -- DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES -- ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD

##### 1. *Applicability, Principle, Interferences, Precision, Bias, and Stability*

1.1 Applicability. The method is applicable to the determination of NO[x] emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations. The lower detectable limit is similar to that for Method 7C. No upper limit has been established; however, when

using the recommended sampling conditions, the method has been found to collect NO<sub>x</sub> emissions quantitatively up to 1782 mg NO<sub>x</sub>/m<sup>3</sup>, as NO<sub>2</sub> (932 pm NO<sub>x</sub>).

1.2 Principle. An integrated gas sample is extracted from the stack and collected in alkaline-potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>3</sub>. Then NO<sub>3</sub> is analyzed by ion chromatography.

1.3 Interferences. Possible interferences are SO<sub>2</sub> and NH<sub>3</sub>. High concentrations of SO<sub>2</sub> could interfere because SO<sub>2</sub> consumes MnO<sub>4</sub> (as does NO<sub>x</sub>) and, therefore, could reduce the NO<sub>x</sub> collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1-percent sulfur coal with no control of SO<sub>2</sub> emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO<sub>2</sub> will reduce the MnO<sub>4</sub> concentration by only 5 percent if all the SO<sub>2</sub> is consumed in the first impinger.

NH<sub>3</sub> is slowly oxidized to NO<sub>3</sub> by the absorbing solution. At 100 ppm NH<sub>3</sub> in the gas stream, an interference of 6 ppm NO<sub>x</sub> (11 mg NO<sub>2</sub>/m<sup>3</sup>) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH<sub>3</sub> injection to control NO<sub>x</sub> emissions unless means are taken to correct the results. An equation has been developed to allow quantitation of the interference and is discussed in Citation 4 of the Bibliography.

1.4 Precision and Bias. The method does not exhibit any bias relative to Method 7. The within-laboratory relative standard deviation for a single measurement was approximately 6 percent at 200 to 270 ppm NO<sub>x</sub>.

1.5 Stability. Collected samples are stable for at least 4 weeks.

## 2. Apparatus

2.1 Sampling and Sample Recovery. The sampling train is the same as in Figure 7C-1 of Method 7C. Component parts are the same as in Method 7C, Section 2.1.

2.2 Sample Preparation and Analysis.

2.2.1 Magnetic Stirrer. With 25- by 10- mm Teflon-coated stirring bars.

2.2.2 Filtering Flask. 500-ml capacity with sidearm.

2.2.3 Buchner Funnel. 75-mm ID. The spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

2.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

2.2.5 Stirring Rods.

2.2.6 Volumetric Flask. 250-ml.

2.2.7 Pipettes. Class A.

2.2.8 Erlenmeyer Flasks. 250-ml.

2.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO<sub>3</sub>, a H<sup>+</sup> suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO<sub>3</sub> is obtained. The system must also be able to resolve and detect

NO<sub>2</sub>.

### 3. Reagents

Unless otherwise indicated, all reagents should 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 Water. Deionized distilled to conform to ASTM Specification D 1193-74, Type 3 (incorporated by reference -- see § 60.17).

3.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of KMnO<sub>4</sub> and 20.0 g of NaOH in 940 ml of water.

#### 3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Hydrogen Peroxide, 5 Percent. Dilute 30 percent H<sub>2</sub>O<sub>2</sub> 1:5 (v/v) with water.

3.2.3 Blank Solution. Dissolve 2.4 g of KMnO<sub>4</sub> and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO<sub>4</sub>/NaOH solution to 100 ml.

3.2.4 KNO<sub>3</sub> Standard Solution. Dry KNO<sub>3</sub> at 110 deg. C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO<sub>3</sub> to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>3</sub> concentration from the following relationship:

$$\mu\text{g NO}_3/\text{ml} = \text{g of KNO}_3 \times 10^{-3} \times 62.01 / 101.10$$

This solution is stable for 2 months without preservative under laboratory conditions.

3.2.5 Eluent, 0.003 M NaHCO<sub>3</sub>/0.0024 M Na<sub>2</sub>CO<sub>3</sub>. Dissolve 1.008 g NaHCO<sub>3</sub> and 1.018 g Na<sub>2</sub>CO<sub>3</sub> in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

3.2.6 Quality Assurance Audit Samples. This is the same as in Method 7, Section 3.3.9. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7D.

### 4. Procedure

4.1 Sampling. This is the same as in Method 7C, Section 4.1.

4.2 Sample Recovery. This is the same as in Method 7C, Section 4.2.

4.3 Sample Preparation for Analysis. Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO<sub>2</sub> is converted to NO<sub>3</sub>. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H<sub>2</sub>O<sub>2</sub> in increments of approximately 5 ml using a 5-ml pipette. When the KMnO<sub>4</sub> color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H<sub>2</sub>O<sub>2</sub> addition is complete. If the KMnO<sub>4</sub> color persists, add more H<sub>2</sub>O<sub>2</sub>, with stirring, until the supernatant liquid is clear. (NOTE: The faster the stirring rate, the less volume of H<sub>2</sub>O<sub>2</sub> that will be required to remove the KMnO<sub>4</sub>.) Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO<sub>3</sub> analysis.

4.4 Sample Analysis. The following chromatographic conditions are recommended: 0.003 M NaHCO<sub>3</sub>/0.0024 M Na<sub>2</sub>CO<sub>3</sub> eluent solution. (3.2.5), full scale range 3  $\mu$  MHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO<sub>3</sub> retention time of approximately 15 minutes (Figure 7D-1).

Figure 7D-1. Ion chromatograph of a prepared sample

[See figure in original]

Establish a stable baseline. Inject a sample of water, and determine if any NO<sub>3</sub> appears in the chromatogram. If NO<sub>3</sub> is present, repeat the water load/injection procedure approximately five times; then re-inject a water sample, and observe the chromatogram. When no NO<sub>3</sub> is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration standards (to compensate for any drift in response of the instrument). Measure the NO<sub>3</sub> peak height or peak area, and determine the sample concentration from the calibration curve.

4.5 Audit analysis. This is the same as in Method 7, Section 4.4.

## 5. Calibration

### 5.1 Dry Gas Metering System (DGM).

5.1.1 Initial Calibration. Same as in Method 6, Section 5.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 3 in the Bibliography be consulted.

5.1.2 Post-Test Calibration Check. Same as in Method 6, Section 5.1.2.

5.2 Thermometers for DGM and Barometer. Same as in Method 6, Section 5.2 and 5.4, respectively.

5.3 Calibration Curve for Ion Chromatograph. Dilute a given volume (1.0 ml or greater) of the KNO<sub>3</sub> standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in Section 4.4. Determine peak height or area, and plot the individual values versus concentration in  $\mu$ gNO<sub>3</sub>/ml. Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

## 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 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, Section 6.1

6.2 Total  $\mu\text{g NO}_2$  Per Sample.

$$m = (S-B) \times 250 \times 1000 / 50 \times 46.01 / 62.01 = 3710 (S-B) \text{ Eq. 7D-1}$$

Where:

$m$  = Mass of  $\text{NO}_x$ , as  $\text{NO}_2$ , in sample,  $\mu\text{g}$ .

$S$  = Analysis of sample,  $\mu\text{g NO}_3/\text{ml}$ .

$B$  = Analysis of blank,  $\mu\text{g NO}_3/\text{ml}$ .

250 = Volume of prepared sample, ml.

46.01 = Molecular weight of  $\text{NO}_2$ .

62.01 = Molecular weight of  $\text{NO}_3$ .

1000 = Total volume of  $\text{KMnO}_4$  solution, ml.

50 = Aliquot  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

6.3 Sample Concentration.

$$C = K_2 \times m / V[m(\text{std})]$$

Where:

$C$  = Concentration of  $\text{NO}_x$  as  $\text{NO}_2$ , dry basis,  $\text{mg/dscm}$ .

$K_2 = 10^{-3} \text{ mg}/\mu\text{g}$ .

$V[m(\text{std})]$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions,  $\text{dscm}$ .

6.4 Conversion Factors.

1.0 ppm  $\text{NO}$  = 1.247  $\text{mg NO}/\text{m}^3$  at STP.

1.0 ppm  $\text{NO}_2$  = 1.912  $\text{mg NO}_2/\text{m}^3$  at STP.

1  $\text{ft}^3 = 2.832 \times 10^{-2} \text{ m}^3$ .

1000  $\text{mg} = 1 \text{ g}$ .

## 7. Quality Control

Quality control procedures are specified in Sections 4.1.3 (flow rate accuracy) and 4.5 (audit analysis accuracy) of Method 7C.

## 8. Bibliography

1. Margeson, J. H., W. J. Mitchell, J. C. Suggs, and M. R. Midgett. Integrated Sampling and Analysis Methods for Determining NO<sub>x</sub> Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. 32:1210-1215. 1982.
2. Memorandum and attachment from J. H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH<sub>3</sub> Interference in Methods 7C and 7D.
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4. Margeson, J. H., et al. An Integrated Method for determining NO<sub>x</sub> Emissions at Nitric Acid Plants. Manuscript submitted to Analytical Chemistry. April 1984.

### METHOD 7E -- DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

#### 1. *Applicability and Principle*

1.1 Applicability. This method is applicable to the determination of nitrogen oxides (NO<sub>x</sub>) concentrations in emissions from stationary sources only when specified within the regulations.

1.2 Principle. A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental chemiluminescent analyzer for determination of NO<sub>x</sub> concentration. Performance specifications and test procedures are provided to ensure reliable data.

#### 2. *Range and Sensitivity*

Same as Method 6C, Sections 2.1 and 2.2.

#### 3. *Definitions*

3.1 Measurement System. The total equipment required for the determination of NO<sub>x</sub> concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface, Gas Analyzer, and Data Recorder. Same as Method 6C, Sections 3.1.1, 3.1.2, and 3.1.3.

3.1.2 NO<sub>2</sub> to NO Converter. A device that converts the nitrogen dioxide (NO<sub>2</sub>) in the sample gas to nitrogen oxide (NO).

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, and Response Time. Same as Method 6C, Sections 3.2 through 3.8.

3.3 Interference Response. The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

#### 4. *Measurement System Performance Specifications*

Same as Method 6C, Sections 4.1 through 4.4.

## 5. Apparatus and Reagents

5.1 Measurement System. Any measurement system for NO<sub>x</sub> that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1 of Method 6C. The essential components of the measurement system are described below:

5.1.1 Sample Probe, Sample Line, Calibration Valve Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder. Same as Method 6C, Sections 5.1.1 through 5.1.9, and 5.1.11.

5.1.2 NO<sub>2</sub> to NO Converter. That portion of the system that converts the nitrogen dioxide (NO<sub>2</sub>) in the sample gas to nitrogen oxide (NO). An NO<sub>2</sub> to NO converter is not necessary if data are presented to demonstrate that the NO<sub>2</sub> portion of the exhaust gas is less than 5 percent of the total NO<sub>x</sub> concentration.

5.1.3 NO<sub>x</sub> Analyzer. An analyzer based on the principles of chemiluminescence, to determine continuously the NO<sub>x</sub> concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer.

5.2 NO<sub>x</sub> Calibration Gases. The calibration gases for the NO<sub>x</sub> analyzer shall be NO in N<sub>2</sub>. Three calibration gases, as specified in Sections 5.3.1 through 5.3.3. of Method 6C, shall be used. Ambient air may be used for the zero gas.

## 6. Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Gas Concentration Verification. Follow Section 6.1 of Method 6C, except if calibration gas analysis is required, use Method 7, and change all 5 percent performance values to 10 percent (or 10 ppm, whichever is greater).

6.2 Interference Response. Conduct an interference response test of the analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response (e.g., changes in the gas detector). Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sample System Bias Check. Follow Sections 6.2 through 6.4 of Method 6C.

6.4 NO<sub>2</sub> to NO Conversion Efficiency. Unless data are presented to demonstrate that the NO<sub>2</sub> concentration within the sample stream is not greater than 5 percent of the NO<sub>x</sub> concentration, conduct an NO<sub>2</sub> to NO conversion efficiency test in accordance with Section 5.6 of Method 20.

## 7. Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 7.

7.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the

same rate as used during the system calibration drift test. Maintain constant rate sampling (i.e., +/-10 percent) during the entire run. The sampling time per run shall be the same as the total time required to perform a run using Method 7, plus twice the system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed, to determine the average effluent concentration.

7.3 Zero and Calibration Drift Test. Follow Section 7.4 of Method 6C.

## 8. *Emission Calculation*

Follow Section 8 of Method 6C.

## 9. *Bibliography*

Same as bibliography of Method 6C.

# 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 determination 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 ( $0.03 \times 10^{-7}$  pounds/cubic foot) for sulfur trioxide and 1.2 mg/m<sup>3</sup> ( $0.74 \times 10^{-7}$  lb/ft<sup>3</sup>) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m<sup>3</sup> (35.3 ft<sup>3</sup>) gas sample is about 12,500 mg/m<sup>3</sup> ( $7.7 \times 10^{-4}$  lb/ft<sup>3</sup>). 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 required.

Filterable particulate matter may be determined along with SO<sub>3</sub> and SO<sub>2</sub> (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 2.1 of Method 6.) If this option is chosen, particulate analysis is gravimetric only; H<sub>2</sub>SO<sub>4</sub> 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 similar 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 available. 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.

[SEE FIGURE IN ORIGINAL]

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.

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 unstricted 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 deg. C (2 deg. 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  $\pm 0.5$  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 +/- 0.5 g.

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  $\text{KMnO}_4$  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 commercial 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 nm. 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-arsenophenylazo) 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 ( $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ) in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol; 1.22 g of barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) 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  $\pm 0.0002$  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

##### 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 use as a blank solution. Place about 200 g 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<sup>3</sup>/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.

## FIGURE 8-2 -- FIELD DATA

[SEE FIGURE IN ORIGINAL]

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 occurred, 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 a 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 thorn 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),  $deg.\ K$  ( $deg.\ R$ ).

$T[s]$  = Average absolute stack gas temperature (see Figure 8-2),  $deg.\ K$  ( $deg.\ R$ ).

$T[std]$  = Standard absolute temperature,  $293\ deg.\ K$  ( $528\ deg.\ R$ ).

$V[a]$  = 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 sulfuric 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.

DELTA H = Average pressure drop across orifice meter, mm (in.) H<sub>2</sub>O.

THETA = 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 deg. C and 760 mm Hg or 68 deg. F and 29.92 in. Hg) by using Equation 8-1.

$V[m(std)] = V[m] Y (T[std] / T[m]) P[bar] + (DELTA H / 13.6) / P[std] = K[i] V[m] Y P[bar] + (DELTA H/13.6) / T[m]$  Equation 8-1

Where:

K[1] = 0.3858 deg. K/mm Hg for metric units.

= 17.64 deg. 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<sub>3</sub>) Concentration.

$$C[\text{H}_2\text{SO}_4] = K[2] N(V[t] - V[tb]) (V[\text{soln}] / V[a] / V[m(\text{std})])$$

Equation 8-2

Where:

$$K[2] = 0.04904 \text{ g/milliequivalent for metric units.}$$

$$= 1.081 \times 10^{-4} \text{ lb/meq for English units.}$$

#### 6.6 Sulfur Dioxide Concentration.

$$C[\text{SO}_2] = K[3] N(V[t] - V[tb]) (V[\text{soln}] / V[a] / V[m(\text{std})])$$

Equation 8-3

Where:

$$K[3] = 0.03203 \text{ g/meq for metric units.}$$

$$= 7.061 \times 10^{-5} \text{ lb/meq for English units.}$$

#### 6.7 Isokinetic Variation.

##### 6.7.1 Calculation from Raw Data.

$$I = 100T[s][K[4]V[1c] + (V[m]Y/T[m])/(P[\text{bar}] + \text{DELTA H}/13.6)] / 60 \text{ THETA } [vs]P[s]A[n]$$

Eq. 8-4

Where:

$$K[4] = 0.003464 \text{ mm Hg-m}^3\text{/ml-deg. K for metric units.}$$

$$= 0.002676 \text{ in. Hg-ft}^3\text{/ml-deg. R for English units.}$$

##### 6.7.2 Calculation from Intermediate Values.

$$I = T[s] V[m(\text{std})] P[\text{std}] 100 / T[\text{std}] v[s] \text{ THETA } A[n] P[s] 60 (1 - B[\text{ws}] = K[5] T[s] V[m(\text{std})] / P[a] v[s] A[n] \text{ THETA } (1 - B[\text{ws}])$$

Equation 8-5

where:

$$K[5] = 4.320 \text{ for metric units.}$$

$$= 0.09450 \text{ for English units}$$

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 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 6.4.

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## 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  $n_1$  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.

$n_1$  For a set, positive error = average opacity determined by observers' 25 observations--average opacity determined from transmissometer's 25 recordings.

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 section 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 deg. 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, a sketch of the observer's position relative to the source, 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.

2.4 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 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 section 3.2. Smoke generators used pursuant to section 3.2 shall be equipped with a smoke meter which meets the requirements of section 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 section 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 section 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-- Citation 3).
c. Angle of view	15 deg. maximum total angle.
d. Angle of projection	15 deg. 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

[SEE FIGURE IN ORIGINAL]

## FIGURE 9-2--OBSERVATION RECORD

[SEE FIGURE IN ORIGINAL]

## FIGURE 9-2--OBSERVATION RECORD--(CONTINUED)

[SEE FIGURE IN ORIGINAL]

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 deg. The total angle of view may be calculated from:  $\theta = 2 \tan^{-1} d / 2L$ , where  $\theta$  = 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 deg. The total angle of projection may be calculated from:  $\theta = 2 \tan^{-1} d / 2L$ , where  $\theta$  = 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. *Bibliography.*

1. Air Pollution Control District Rules and Regulations, Los Angeles County Air Pollution Control District, Regulation IV, Prohibitions, Rule 50.
2. Weisburd, Melvin I., Field Operations and Enforcement Manual for Air, U.S. Environmental Protection Agency, Research Triangle Park, NC. APTD-1100, August 1972, pp. 4.1-4.36.
3. Condon, E.U., and Odishaw, H., Handbook of Physics, McGraw-Hill Co., New York, NY, 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[0]) 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):

$$D(\text{lidar}) = A + R \phi \leq 0.75 D(\text{Plume}) \quad (\text{AM1-1})$$

Where:

D(Plume)=diameter of the plume (cm),

$\phi$  =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  $\pm 15$  deg. (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  $\pm 6\%$  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  $\pm 3\%$  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 deg. 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  $S[In]$  (near region standard deviation, Equation

AM1-5) or S[If] (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 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.

Figure AM1-I Lidar Log Control Number Tabulation

[SEE FIGURE IN ORIGINAL]

[SEE FIGURE IN ORIGINAL]

[SEE FIGURE IN ORIGINAL]

(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.

SOURCE: [36 FR 24877, Dec. 23, 1971]

AUTHORITY: 42 U.S.C. 7401, 7411, 7414, 7416, and 7601.

Title 40 -- Protection of Environment; Revised as of July 1, 1991

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

**40 CFR 60. Appendix A** to Part 60

Figure AM1-III. Plots of Lidar Backscatter Signals

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.)

$$O[p]=(100\%) \times [1 - (I[f] / R[f] \times R[n] / I[n])^{1/2}], \text{ (AM1-2)}$$

Where:

$I[n]$ =near-region pick interval signal amplitude, plume signal,  $1/R^{1/2}$  corrected,

$I[f]$ =far-region pick interval signal amplitude, plume signal,  $1/R^{1/2}$  corrected,

$R[n]$ =near-region pick interval signal amplitude, reference signal,  $1/R^{1/2}$  corrected, and

$R[f]$  =far-region pick interval signal amplitude, reference signal,  $1/R^{1/2}$  corrected.

The  $1/R^{1/2}$  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.

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  $1/R^{1/2}$ . The amplitude of  $I[n]$  shall be calculated according to Equation (AM-3).

$$I[n] = 1/n \times \langle m \rangle \text{ SIGMA } [i = 1] \times I[ni], \text{ (AM1-3)}$$

Where:

$I[ni]$  = the amplitude of the  $i$ th sample interval (near-region),

$\text{SIGMA}$  = 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).

$$I[f] = 1/m \times \langle m \rangle \text{ SIGMA } [i = 1] \times I[fi], R[n] = 1/m \times \langle m \rangle \text{ SIGMA } [i = 1] \times R[ni], R[f] = 1/m \times \langle m \rangle \text{ SIGMA } [i = 1] \times R[fi].$$

(AM1-4)

The standard deviation,  $S[I_n]$ , of the set of amplitudes for the near-region pick interval,  $I[n]$ , shall be calculated using Equation (AM1-5).

Similarly, the standard deviations  $S[I_f]$ ,  $S[R_n]$ , and  $S[R_f]$  are calculated with the three expressions in Equation (AM1-6).

$$S[I_n] = [\langle m \rangle \text{ SIGMA } [i = 1] \times (I[ni] - I[n])^2 / (m - 1)]^{1/2} * S[I_f] = [\langle m \rangle \text{ SIGMA } [i = 1] \times (I[fi] - I[f])^2 / (m - 1)]^{1/2}$$

(AM1-5)

$$S[R_n] = [\langle m \rangle \text{ SIGMA } [i = m] \times (R[ni] - R[n])^2 / (m - 1)]^{1/2},$$

$$S[R_f] = [\langle m \rangle \text{ SIGMA } [i = m] \times (R[fi] - R[f])^2 / (m - 1)]^{1/2}.$$

(AM1-6)

The standard deviation,  $S[o]$ , for each associated opacity value,  $O[p]$ , shall be calculated using Equation (AM1-7).

$$S[o] = (100\%) / 2 \times (I[f] / R[f] \times R[n] / I[n])^{1/2} \times [S[I_n]^2 / I[n]^2 + S[I_f]^2 / I[f]^2 + S[R_n]^2 / R[n]^2 + S[R_f]^2 / R[f]^2]^{1/2}$$

(AM1-7)

The calculated values of  $I[n]$ ,  $I[f]$ ,  $R[n]$ ,  $R[f]$ ,  $S[I_n]$ ,  $S[I_f]$ ,  $S[R_n]$ ,  $S[R_f]$ ,  $O[p]$ , 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 epsilon 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).

$$O[pc] = (100\%) \times [1 - (1 - 0.01 O[p]) \langle \cos X (\pi / 2 - \epsilon) \rangle] = (100\%) \times [1 - 0.01 O[p] \langle \sin \epsilon \rangle]$$

(AM1-8)

The correction in Equation (AM1-8) shall be performed if the inequality in Equation (AM1-9) is true.

$$\epsilon \geq \sin^{-1} \left[ \frac{101 - O[p]}{100 - O[p]} \right]$$

AM1-9)

Figure AM1-IV(a) shows the geometry used to calculate epsilon 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.

[SEE FIGURE IN ORIGINAL]

R[s]=range from lidar to source n\*

BETA[s]=elevation angle of R[s] n\*

R[p]=range from lidar to plume at the opacity measurement point n\*

BETA[p]=elevation angle of R[p] n\*

R[a]=range from lidar to plume at some arbitrary point, P[a], so the drift angle of the plume can be determined n\*

BETA[a]=elevation angle of R[a] n\*

alpha=angle between R[p] and R[a]

n\* Obtained directly from lidar. These values should be recorded.

R's=projection of R[s] in the horizontal plane

R'p=projection of R[p] in the horizontal plane

R's=projection of R[a] in the horizontal plane

PSI'=angle between R'[s] and R'[p] n\*

alpha'=angle between R'[p] and R'[a] n\*

R</= =distance from the source to the opacity measurement point projected in the horizontal plane

R THETA =distance from opacity measurement point P[p] to the point in the plume P[a].

n\* Obtained directly from lidar. These values should be recorded.

$$O[pc] = 1 - (1 - O[p]) \cos \epsilon = 1 - (1 - O[p]) \sin \epsilon$$

(AMI-8)

The correction angle epsilon shall be determined using Equation AMI-10.

Where:

alpha - Cos<-1> (COS BETA[p] COS BETA[a] COS alpha' + Sin BETA[p] Sin BETA[a], and

$$R \text{ THETA} = (R[p]^2 + R[a]^2 - 2 R[p] R[a] \cos \alpha)^{1/2}$$

R</=, the distance from the source to the opacity measurement point projected in the horizontal plane, shall be determined using Equation AM1-11.

$$R(\sigma) = (R'[s]^2 + R'[p]^2 - 2R'[s] R'[p] \cos \psi)^{1/2},$$

(AM1-11)

Where:

R'[s]=R[s] COS BETA[s], and

R'[p]=R[p] 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 epsilon instead of Equation AM1-10.

$$\epsilon = \cos^{-1} X [R[p]^2 + R[\sigma]^2 - R'[s]^2 / 2 R[p] R[\sigma]]$$

(AM1-12)

Where:

$$R''[s] = (R'[p]^2 \sin^2 \beta[p])^{1/2}.$$

If the angle epsilon is such that epsilon </- 30 deg. or epsilon >/- 150 deg., 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, BETA[p] [Figure AM1-V], is greater than or equal to the value calculated in Equation AM1-13.

$$\beta[p] >/- \cos^{-1} X [\ln X (101 - O[p]) / \ln X (100 - O[p])]$$

(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).

$$O[pc] = (100\%) \times [1 - (1 - 0.01 O[p])^{\cos \beta}],$$

(AM1-14)

Where:

BETA[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 BETA[p], O[p] and O[pc] should be recorded.

[SEE FIGURE IN ORIGINAL]

2.6.3 Determination of Actual Plume Opacity. Actual opacity of the plume shall be determined by Equation AM1-15.

$$O[pa] = O[pc] - [2S[o] + 5\%].$$

(AM1-15)

2.6.4 Calculation of Average Actual Plume Opacity. The average of the actual plume opacity, O[pa], shall be calculated as the average of the consecutive individual actual opacity values, O[pa], by Equation AM1-16.

$$O[pa] = 1 / n \times \sum_{k=1}^n (O[pa])[k],$$

(AM1-16)

Where:

(O[pa])[k]=the kth actual opacity value in an averaging interval containing n opacity values; k is a summing index.

SIGMA =the sum of the individual actual opacity values.

n=the number of individual actual opacity values contained in the averaging interval.

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 performed 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.

[SEE FIGURE IN ORIGINAL]

Figure AM1-VI. Test Configuration for Technique 1.

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.

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 ( $I[f]$ ), dividing it by the 0% opacity signal level ( $I[n]$ ) 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.

### 3.3.1 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 with +/- 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.

[SEE FIGURE IN ORIGINAL]

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, March 8, 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.

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<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) are 3.5 percent H<sub>2</sub>O per 7 ppm CO and 10 percent CO<sub>2</sub> 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<sub>2</sub>O per 25 ppm CO and 10 percent CO<sub>2</sub> 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 n1 glass, equipped with a filter to remove particulate matter.

n1 Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

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 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 ft<sup>3</sup>). 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 10-2. Integrated gas sampling train.

[SEE FIGURES IN ORIGINAL]

5.3.5 CO<sub>2</sub> 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<sub>2</sub>) for instrument span, prepurified grade of N<sub>2</sub> 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.

Figure 10-3. Analytical equipment.

[SEE FIGURE IN ORIGINAL]

6.2 Silica Gel. Indicating type, 6 to 16 mesh, dried at 175 deg. C (347 deg. F) for 2 hours.

6.3 Ascarite. Commercially available.

## 7. Procedure

## 7.1 Sampling.

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<sub>2</sub> content of the gas may be determined by using the Method 3 integrated sample procedure, or by weighing the ascarite CO<sub>2</sub> removal tube and computing CO<sub>2</sub> 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<sub>2</sub> content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO<sub>2</sub> removal tube and computing CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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	
	Rotameter setting, liters per
Clock time	minute (cubic feet per minute)

## 9. Calculation

Calculate the concentration of carbon monoxide in the stack using Equation 10-1.

$$C[\text{CO stack}] = C[\text{CO NDIR}] \times (1 - F[\text{CO}_2])$$

Eq. 10-1

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*

1. McElroy, Frank, The Intertech NDIR-CO Analyzer, Presented at 11th Methods Conference on Air Pollution, University of California, Berkeley, CA. April 1, 1970.
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.
3. MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Technical Products Division, Pittsburgh, PA.
4. Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instruments, Inc., Beckman Instructions 1635-B, Fullerton, CA. October 1967.
5. Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton, NJ.
6. UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, WV

## 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[2])  -- 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 10A -- DETERMINATION OF CARBON MONOXIDE EMISSIONS IN CERTIFYING CONTINUOUS EMISSION MONITORING SYSTEMS AT PETROLEUM REFINERIES

### 1. Applicability and Principle

*1.1 Applicability.* This method applies to the measurement of carbon monoxide (CO) at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS's) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators [40 CFR Part 60.105(a)(2)].

*1.2 Principle.* An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur and nitrogen oxides, and collected in a Tedlar bag. The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with p-sulfaminobenzoic acid.

*1.3. Range and Sensitivity.*

*1.3.1 Range.* Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

*1.3.2 Sensitivity.* The detection limit is 3 ppm based on three times the standard deviation of the mean reagent blank values.

*1.4 Interferences.* Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO<sub>2</sub>) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

*1.5 Precision, Accuracy, and Stability.*

*1.5.1 Precision.* The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

*1.5.2 Accuracy.* The method contains no significant biases when compared to an NDIR analyzer calibrated with National Bureau of Standards (NBS) standards.

*1.5.3 Stability.* The individual components of the colorimetric reagent are stable for at least 1 month. The colorimetric reagent must be used within 2 days after preparation to avoid excessive blank correction. The samples in the Tedlar bag should be stable for at least 1 week if the bags are leak-free.

n1 Mention of trade names or commercial products in this publication does not constitute the endorsement or recommendation for use by the Environmental Protection Agency.

## *2. Apparatus*

*2.1 Sampling.* The sampling train is shown in Figure 10A-1, and component parts are discussed below:

Figure 10A-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

*2.1.1 Probe.* Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

*2.1.2 Sample Conditioning System.* Three Greenburg-Smith impingers connected in series with leak-free connections.

2.1.3 *Pump*. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min to the flexible bag.

2.1.4 *Surge Tank*. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

2.1.5 *Rate Meter*. Rotameter, or equivalent, to measure flow rate at 300 ml/min. Calibrate according to Section 5.2.

2.1.6 *Flexible Bag*. Tedlar, or equivalent, with a capacity of 10 liters and equipped with a sealing quick-connect plug. The bag must be leak-free according to Section 4.1. For protection, it is recommended that the bag be enclosed with a rigid container.

2.1.7 *Valves*. Stainless-steel needle valve to adjust flow rate, and stainless-steel three-way valve, or equivalent.

2.1.8 *CO[2] Analyzer*. Method 3 or its approved alternative to measure CO[2] concentration to within 0.5 percent.

2.1.9 *Volume Meter*. Dry gas meter, calibrated and capable of measuring the sample volume under rotameter calibration conditions of 300 ml/min for 10 minutes

2.1.10 *Pressure Gauge*. A water filled U-tube manometer, or equivalent, of about 28 cm (12 in.) to leak-check the flexible bag.

## 2.2 *Analysis*.

2.2.1 *Spectrophotometer*. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

2.2.2 *Spectrophotometer Cells*. 1-cm path-length.

2.2.3 *Vacuum Gauge*. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

2.2.4 *Pump*. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

2.2.5 *Barometer*. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.6 *Reaction Bulbs*. Pyrex glass, 100.ml with Teflon stopcock (Figure 10A-2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2-2161 may also be used.

Figure 10A-2. Sample reaction bulbs.

[SEE FIGURE IN ORIGINAL]

2.2.7 *Mainfold*. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A-3.

2.2.8 *Pipets*. Class A, 10-ml size.

2.2.9 *Shaker Table*. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A-4).

2.2.10 *Valve*. Stainless steel shut-off valve.

Figure 10A-3. Sample bulb filling system.

[SEE FIGURE IN ORIGINAL]

2.2.11 *Analytical Balance*. Capable of accurately weighing to 0.1 mg.

### 3. Reagents

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

#### 3.1 Sampling.

3.1.1 *Water*. Deionized distilled, as described in Method 6, Section 3.1.1.

3.1.2 *Alkaline Permanganate Solution, 0.25 M KMnO<sub>4</sub> / 1.5 M NaOH*. Dissolve 40 g KMnO<sub>4</sub> and 60 g NaOH in water, and dilute to 1 liter.

#### 3.2 Analysis.

3.2.1 *Water*. Same as in Section 3.1.1.

3.2.2 *1 M Sodium Hydroxide (NaOH) Solution*. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

3.2.3 *0.1 M Silver Nitrate (AgNO<sub>3</sub>) Solution*. Dissolve 8.5 g AgNO<sub>3</sub> in water, and dilute to 500 ml.

3.2.4 *0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution*. Dissolve 10.0 g p-SABA in 0.1 M NaOH (prepared by diluting 50 ml of 1 M NaOH to 500 ml), and dilute to 500 ml with 0.1 M NaOH.

Figure 10A-4. Shaker table adapter.

[SEE FIGURE IN ORIGINAL]

3.2.5 *Colorimetric Solution*. To a flask, add 100 ml of p-SABA solution and 100 ml of AgNO<sub>3</sub> solution. Mix, and add 50 ml of 1 M NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

3.2.6 *Standard Gas Mixtures*. Traceable to NBS standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 5.3).

The calibration gases shall be certified by the manufacturer to be within 2 percent of the specified

concentrations.

#### 4. Procedure

**4.1 Sample Bag Leak-checks.** While a bag leak-check is required after bag use, it should also be done before the bag is used for sample collection. The bag should be leak-checked in the inflated and deflated condition according to the following procedures.

Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak. Now, evacuate the bag with a leakless pump that is connected on the downstream side of a flow-indicating device such as a 0-to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

**4.2 Sampling.** Evacuate the Tedlar bag completely using a vacuum pump. Assemble the apparatus as shown in Figure 10A-1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and three-way valve. Do not connect the Tedlar bag to the system at this time.

Leak-check the sampling system by placing a vacuum gauge at or near the probe inlet, plugging the probe inlet, opening the three-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

Purge the system with sample gas by inserting the probe into the stack and drawing sample through the system at 300 ml/min +/- 10 percent for 5 minutes. Connect the evacuated Tedlar bag to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the Tedlar bag is nearly full. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

The scrubbing solution is adequate for removing sulfur and nitrogen oxides from 50 liters of stack gas when the concentration of each is less than 1,000 ppm and the CO<sub>2</sub> concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

**4.3 Carbon Dioxide Measurement.** Measure the CO<sub>2</sub> content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

**4.4 Analysis.** Assemble the system shown in Figure 10A-3, and record the information required in Table 10A-1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the Tedlar bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm, proceed as described below. If a leak is present, find and correct it before proceeding further.

TABLE 10A-1. DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPLICATE

Sample no./	Room temp.	Stack %	Bulb vol.,	Reagent vol. in	Partial pressure of gas in
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Type	deg. C	CO[2] no. liters	bulb, liter	bulb mm Hg
Blank				
Std. 1				
Std. 2				
Sample 1				
Sample 2				
Sample 3				

Sample no./ Type	Shaking P[bar], mm Hg	Abs time, min	Abs versus water	Avg. A - A[r] A[s] A[s]
Blank				
Std. 1				
Std. 2				
Sample 1				
Sample 2				
Sample 3				

Blank  
Std. 1  
Std. 2  
Sample 1  
Sample 2  
Sample 3

Record the vacuum pressure (P [v]) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the Tedlar bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the Tedlar bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure (P[bar], to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

Immediately after shaking, measure the absorbance (A) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or at 600 nm if the concentration is above 400 ppm. This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell several times between samples with water.

Prepare and analyze standards and a reagent blank as described in Section 5.3. Use water as the reference.

Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed. Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in Section 5.3.

## 5. Calibration

**5.1 Bulb Calibration.** Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water (at the measurement temperature). Record the volume on the bulb; alternatively, mark an identification number on the bulb, and record the volume in a notebook.

**5.2 Rate Meter Calibration.** Assemble the system as shown in Figure 10A-1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull gas through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to determine the volume of gas that passed through the system.

**5.3 Spectrophotometer Calibration Curve.** The calibration curve is established by taking at least two sets of three bulbs of known CO collected from Tedlar bags through the analysis procedure. Reject the standard set where any of the individual bulb absorbances differ from the set mean by more than 10 percent. Collect the standards as described in Section 4.2. Prepare standards to span the 0- to 400- or 400- to 1000-ppm range. If any samples span both concentration ranges, prepare a calibration curve for each range. A set of three bulbs containing colorimetric reagent but no CO should serve as a reagent blank and be taken through the analysis procedure.

Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A-1 and Table 10A-1. Construct a graph of average absorbance for each standard against its corresponding concentration in ppm. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in Section 1.3.1.

## 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.

A = Sample absorbance, uncorrected for the reagent blank.

A[r] = Absorbance of the reagent blank.

A[s] = Average sample absorbance per liter, units/liter.

B[w] = Moisture content in the bag sample.

C = CO concentration in the stack gas, dry basis, ppm.

C[b] = CO concentration of the bag sample, dry basis, ppm.

C[g] = CO concentration from the calibration curve, ppm.

F = Volume fraction of CO<sub>2</sub> in the stack.

n = Number of reaction bulbs used per bag sample.

P[bar] = Barometric pressure, mm Hg.

P[v] = Residual pressure in the sample bulb after evacuation, mm Hg.

P[w] = Vapor pressure of H<sub>2</sub>O in the bag (from Table 10A-2), mm Hg.

V[b] = Volume of the sample bulb, liters.

V[r] = Volume of reagent added to the sample bulb, 0.0100 liter.

### 6.2 Average Sample Absorbance per Liter.

Average the three absorbance values for each bulb set. Then calculate A[s] for each set of gas bulbs using Equation 10A-1. Use A[s] to determine the CO concentration from the calibration curve (C[g]).

$$A[s] = (A - A[r]) (P[\text{bar}]) / (V[b] - V[r]) (P[\text{bar}] - P[v])$$

Eq. 10A-1

NOTE: A and A[r] must be at the same wavelength.

### 6.3 CO Concentration in the Bag.

Calculate C[b] using Equations 10A-2 and 10A-3. If condensate is visible in the Tedlar bag, calculate B[w] using Table 10A-2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B[w] using the temperature and barometric pressure recorded at the sampling site.

$$B[w] = P[w] / P[\text{bar}]$$

Eq. 10A-2

$$C[b] = C[g] / (1 - B[w])$$

Eq. 10A-3

### 6.4 CO Concentration in the Stack.

$$C = C[b] (1 - F)$$

Eq. 10A-4

TABLE 10A-2. MOISTURE CORRECTION

Temperature, deg. C	Vapor pressure of H <sub>2</sub> O, mm Hg	Temperature, deg. C	Vapor pressure of H <sub>2</sub> O, mm Hg
------------------------	--	------------------------	--

4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

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## METHOD 10B -- DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

### *1. Applicability and Principle*

1.1 Applicability. This method applies to the measurement of carbon monoxide (CO) emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

1.2 Principle. An integrated gas sample is extracted from the sampling point and analyzed for CO. The sample is passed through a conditioning system to remove interferences and collected in a Tedlar bag. The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH<sub>4</sub>) prior to analysis by flame ionization detection FID. The analytical portion of this method is identical to applicable sections in Method 25 detailing CO measurement. The oxidation catalyst required in Method 25 is not needed for sample analysis. Complete Method 25 analytical systems are acceptable alternatives when calibrated for CO and operated by the Method 25 analytical procedures.

NOTE: Mention of trade names or commercial products in this method does not constitute the endorsement or

recommendation for use by the Environmental Protection Agency.

1.3 Interferences. Carbon dioxide (CO<sub>2</sub>) and organics potentially can interfere with the analysis. Carbon dioxide is primarily removed from the sample by the alkaline permanganate conditioning system; any residual CO<sub>2</sub> and organics are separated from the CO by GC.

## 2. Apparatus

2.1 Sampling. Same as in Method 10A, section 2.1.

2.2 Analysis.

2.2.1 Gas Chromatographic (GC) Analyzer. A semicontinuous GC/FID analyzer capable of quantifying CO in the sample and containing at least the following major components.

2.2.1.1 Separation Column. A column that separates CO from CO<sub>2</sub> and organic compounds that may be present. A 1/8-in. OD stainless-steel column packed with 5.5 ft of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose. The column listed in Addendum 1 of Method 25 is also acceptable.

2.2.1.2 Reduction Catalyst. Same as in Method 25, section 2.3.2.

2.2.1.3 Sample Injection System. Same as in Method 25, section 2.3.4, equipped to accept a sample line from the Tedlar bag.

2.2.1.4 Flame Ionization Detector. Linearity meeting the specifications in section 2.3.5.1 of Method 25 where the linearity check is carried out using standard gases containing 20-, 200-, and 1,000-ppm CO. The minimal instrument range shall span 10 to 1,000 ppm CO.

2.2.1.5 Data Recording System. Same as in Method 25, section 2.3.6.

## 3. Reagents

3.1 Sampling. Same as in Method 10A, section 3.1.

3.2 Analysis.

3.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, sections 3.2.1, 3.2.2, and 3.2.3.

3.2.2 Linearity and Calibration Gases. Three standard gases with nominal CO concentrations of 20-, 200-, and 1,000 ppm CO in nitrogen.

3.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH<sub>4</sub> gas with a concentration of 1,000 ppm in air.

## 4. Procedure

4.1 Sample Bag Leak-checks, Sampling, and CO<sub>2</sub> Measurement. Same as in Method 10A, sections 4.1, 4.2, and 4.3.

4.2 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in section 5. Establish an appropriate carrier flow rate and detector temperature for the specific

instrument used.

4.3 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to section 6.2.

## 5. Calibration

5.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to section 4.3 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

5.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000-ppm CH<sub>4</sub> gas (section 3.2.3) to calibrate the analyzer. Repeat the procedure using 1,000-ppm CO (section 3.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

5.3 Analyzer Linearity Check and Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in section 3.2.2. Make triplicate injections of each calibration gas, and then calculate the average response factor (area/ppm) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in section 6.9 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

## 6. Calculations

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

### 6.1 Nomenclature.

A = Average sample area.

B[w] = Moisture content in the bag sample, fraction.

C = CO concentration in the stack gas, dry basis, ppm.

C[b] = CO concentration in the bag sample, dry basis, ppm.

F = Volume fraction of CO<sub>2</sub> in the stack, fraction.

P[bar] = Barometric pressure, mm Hg.

P[w] = Vapor pressure H<sub>2</sub>O in the bag (from Table 10-2, Method 10A), mm Hg.

R = Mean calibration response factor, area/ppm.

6.2 CO Concentration in the Bag. Calculate C[b] using Equations 10B-1 and 10B-2. If condensate is visible in the Tedlar bag, calculate B[w] using Table 10A-1 of Method 10A and the temperature and barometric pressure

in the analysis room. If condensate is not visible, calculate B[w] using the temperature and barometric pressure at the sampling site.

$$B[w] = P[w] / P[\text{bar}]$$

Eq. 10B-1

$$C[b] = A / R(1-B[w])$$

Eq. 10B-2

6.3 CO Concentration in the Stack.

$$C = C[b] (1-F)$$

Eq. 10B-3

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## METHOD 11 -- DETERMINATION OF HYDROGEN SULFIDE CONTENT OF FUEL GAS STREAMS IN PETROLEUM REFINERIES

### 1. Principle and Applicability

1.1 Principle. Hydrogen sulfide (H<sub>2</sub>S) is collected from a source in a series of midget impingers and absorbed in pH 3.0 cadmium sulfate (CdSO<sub>4</sub>) solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO<sub>2</sub> as an interfering species. This method is a revision of the H<sub>2</sub>S method originally published in the FEDERAL REGISTER, Volume 39, No. 47, dated Friday, March 8, 1974.

1.2 Applicability. This method is applicable for the determination of the hydrogen sulfide content of fuel gas streams at petroleum refineries.

### 2. Range and Sensitivity

The lower limit of detection is approximately 8 mg/m<sup>3</sup> (6 ppm). The maximum of the range is 740 mg/m<sup>3</sup> (520 ppm).

### 3. Interferences

Any compound that reduces iodine or oxidizes iodide ion will interfere in this procedure, provided it is collected in the cadmium sulfate impingers. Sulfur dioxide in concentrations of up to 2,600 mg/m<sup>3</sup> is eliminated by the hydrogen peroxide solution. Thiols precipitate with hydrogen sulfide. In the absence of H<sub>2</sub>S, only co-traces of thiols are collected. When methane- and ethane-thiols at a total level of 300 mg/m<sup>3</sup> are present in addition to H<sub>2</sub>S, the results vary from 2 percent low at an H<sub>2</sub>S concentration of 400 mg/m<sup>3</sup> to 14 percent high at an H<sub>2</sub>S concentration of 100 mg/m<sup>3</sup>. Carbon oxysulfide at a concentration of 20 percent does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3 percent, respectively, do not interfere.

Entrained hydrogen peroxide produces a negative interference equivalent to 100 percent of that of an equimolar quantity of hydrogen sulfide. Avoid the ejection of hydrogen peroxide into the cadmium sulfate impingers.

#### 4. Precision and Accuracy

Collaborative testing has shown the within-laboratory coefficient of variation to be 2.2 percent and the overall coefficient of variation to be 5 percent. The method bias was shown to be -4.8 percent when only H<sub>2</sub>S was present. In the presence of the interferences cited in section 3, the bias was positive at low H<sub>2</sub>S concentration and negative at higher concentrations. At 230 mg H<sub>2</sub>S/m<sup>3</sup>, the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

#### 5. Apparatus

##### 5.1 Sampling Apparatus.

5.1.1 Sampling Line. Six to 7 mm (1/4 in.) Teflon n1 tubing to connect the sampling train to the sampling valve.

n1 Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

5.1.2 Impingers. Five midjet impingers, each with 30 ml capacity. The internal diameter of the impinger tip must be 1 mm +/- 0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

5.1.3 Tubing. Glass or Teflon connecting tubing for the impingers.

5.1.4 Ice Bath Container. To maintain absorbing solution at a low temperature.

5.1.5 Drying Tube. Tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at 175 deg. C (350 deg. 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 approval of the Administrator.

NOTE: Do not use more than 30 g of silica gel. Silica gel absorbs gases such as propane from the fuel gas stream, and use of excessive amounts of silica gel could result in errors in the determination of sample volume.

5.1.6 Sampling Valve. Needle valve or equivalent to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

5.1.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate (approx. 1.0 liter/min) and conditions actually encountered during sampling. The meter shall be equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3 deg. C (5.4 deg. F). The gas meter should have a petcock, or equivalent, on the outlet

connector which can be closed during the leak check. Gas volume for one revolution of the meter must not be more than 10 liters.

5.1.8 Flow Meter. Rotameter or equivalent, to measure flow rates in the range from 0.5 to 2 liters/min (1 to 4 cfh).

5.1.9 Graduated Cylinder, 25 ml size.

5.1.10 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 the 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.

5.1.11 U-tube Manometer. 0-30 cm water column. For leak check procedure.

5.1.12 Rubber Squeeze Bulb. To pressurize train for leak check.

5.1.13 Tee, Pinchclamp, and Connecting Tubing. For leak check.

5.1.14 Pump. Diaphragm pump, or equivalent. Insert a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter. The pump is used for the air purge at the end of the sample run; the pump is not ordinarily used during sampling, because fuel gas streams are usually sufficiently pressurized to force sample gas through the train at the required flow rate. The pump need not be leak-free unless it is used for sampling.

5.1.15 Needle Valve or Critical Orifice. To set air purge flow to 1 liter/min.

5.1.16 Tube Packed With Active Carbon. To filter air during purge.

5.1.17 Volumetric Flask. One 1,000 ml.

5.1.18 Volumetric Pipette. One 15 ml.

5.1.19 Pressure-Reduction Regulator. Depending on the sampling stream pressure, a pressure-reduction regulator may be needed to reduce the pressure of the gas stream entering the Teflon sample line to a safe level.

5.1.20 Cold Trap. If condensed water or amine is present in the sample stream, a corrosion-resistant cold trap shall be used immediately after the sample tap. The trap shall not be operated below 0 deg. C (32 deg. F) to avoid condensation of C[3] or C[4] hydrocarbons.

5.2 Sample Recovery.

5.2.1 Sample Container. Iodine flask, glass-stoppered: 500 ml size.

5.2.2 Pipette. 50 ml volumetric type.

5.2.3 Graduated Cylinders. One each 25 and 250 ml.

5.2.4 Flasks. 125 ml, Erlenmeyer.

5.2.5 Wash Bottle.

5.2.6 Volumetric Flasks. Three 1,000 ml.

5.3 Analysis.

5.3.1 Flask. 500 ml glass-stoppered iodine flask.

5.3.2 Burette. 50 ml.

5.3.3 Flask. 125 ml, Erlenmeyer.

5.3.4 Pipettes, Volumetric. One 25 ml; two each 50 and 100 ml.

5.3.5 Volumetric Flasks. One 1,000 ml; two 500 ml.

5.3.6 Graduated Cylinders. One each 10 and 100 ml.

## 6. 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 best available grade.

### 6.1 Sampling.

6.1.1 Cadmium Sulfate Absorbing Solution. Dissolve 41 g of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately  $\frac{3}{4}$  liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be  $3 \pm 0.1$ . Add 10 drops of Dow-Corning Antifoam B. Shake well before use. If Antifoam B is not used, the alternative acidified iodine extraction procedure (Section 7.2.2) must be used.

6.1.2 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide to 3 percent as needed. Prepare fresh daily.

6.1.3 Water. Deionized, distilled to conform to ASTM specifications D1193-72, Type 3. At the option of the analyst, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

### 6.2 Sample Recovery.

6.2.1 Hydrochloric Acid Solution (HCl), 3M. Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of deionized, distilled water in a 1-liter volumetric flask. Dilute to 1 liter with deionized water. Mix thoroughly.

6.2.2 Iodine Solution 0.1 N. Dissolve 24 g of potassium iodide (KI) in 30 ml of deionized, distilled water. Add 12.7 g of resublimed iodine ( $\text{I}_2$ ) to the potassium iodide solution. Shake the mixture until the iodine is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with deionized, distilled water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

6.2.3 Standard Iodine Solution, 0.01 N. Pipette 100.0 ml of the 0.1 N iodine solution into a 1-liter volumetric flask and dilute to volume with deionized, distilled water. Standardize daily as in Section 8.1.1. This solution

must be protected from light. Reagent bottles and flasks must be kept tightly stoppered.

### 6.3 Analysis.

6.3.1 Sodium Thiosulfate Solution, Standard 0.1 N. Dissolve 24.8 g of sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) or 15.8 g of anhydrous sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) in 1 liter of deionized, distilled water and add 0.01 g of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 0.4 ml of chloroform ( $\text{CHCl}_3$ ) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 minutes and store in a glass-stoppered, reagent bottle. Standardize as in Section 8.1.2.

6.3.2 Sodium Thiosulfate Solution, Standard 0.01 N. Pipette 50.0 ml of the standard 0.1 N thiosulfate solution into a volumetric flask and dilute to 500 ml with distilled water.

NOTE: A 0.01 N phenylarsine oxide solution may be prepared instead of 0.01 N thiosulfate (see Section 6.3.3).

6.3.3 Phenylarsine Oxide Solution, Standard 0.01 N. Dissolve 1.80 g of phenylarsine oxide ( $\text{C}_6\text{H}_5\text{AsO}$ ) in 150 ml of 0.3 N sodium hydroxide. After settling, decant 140 ml of this solution into 800 ml of distilled water. Bring the solution to pH 6-7 with 6N hydrochloric acid and dilute to 1 liter. Standardize as in Section 8.1.3.

6.3.4 Starch Indicator Solution. Suspend 10 g of soluble starch in 100 ml of deionized, distilled water and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved, dilute with 900 ml of deionized distilled water and let stand for 1 hour. Neutralize the alkali with concentrated hydrochloric acid, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.

NOTE: Test starch indicator solution for decomposition by titrating, with 0.01 N iodine solution, 4 ml of starch solution in 200 ml of distilled water that contains 1 g potassium iodide. If more than 4 drops of the 0.01 N iodine solution are required to obtain the blue color, a fresh solution must be prepared.

## 7. Procedure

### 7.1 Sampling.

7.1.1 Assemble the sampling train as shown in Figure 11-1, connecting the five midjet impingers in series. Place 15 ml of 3 percent hydrogen peroxide solution in the first impinger. Leave the second impinger empty. Place 15 ml of the cadmium sulfate absorbing solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice bath container and place crushed ice around the impingers. Add more ice during the run, if needed.

7.1.2 Connect the rubber bulb and manometer to first impinger, as shown in Figure 11-1. Close the petcock on the dry gas meter outlet. Pressurize the train to 25-cm water pressure with the bulb and close off tubing connected to rubber bulb. The train must hold a 25-cm water pressure with not more than a 1-cm drop in pressure in a 1-minute interval. Stopcock grease is acceptable for sealing ground glass joints.

NOTE: This leak check procedure is optional at the beginning of the sample run, but is mandatory at the conclusion. Note also that if the pump is used for sampling, it is recommended (but not required) that the pump be leak-checked separately, using a method consistent with the leak-check procedure for diaphragm pumps outlined in Section 4.1.2 of Method 6, 40 CFR part 60, appendix A.

7.1.3 Purge the connecting line between the sampling valve and first impinger, by disconnecting the line from the first impinger, opening the sampling valve, and allowing process gas to flow through the line for a minute or two. Then, close the sampling valve and reconnect the line to the impinger train. Open the petcock on the dry gas meter outlet. Record the initial dry gas meter reading.

Figure 11-1. H<sub>2</sub>S sampling train.

[SEE FIGURE IN ORIGINAL]

7.1.4 Open the sampling valve and then adjust the valve to obtain a rate of approximately 1 liter/min. Maintain a constant (+/- 10 percent) flow rate during the test. Record the meter temperature.

7.1.5 Sample for at least 10 min. At the end of the sampling time, close the sampling valve and record the final volume and temperature readings. Conduct a leak check as described in Section 7.1.2 above.

7.1.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump, as shown in Figure 11-1. Purge the train (at a rate of 1 liter/min) with clean ambient air for 15 minutes to ensure that all H<sub>2</sub>S is removed from the hydrogen peroxide. For sample recovery, cap the open ends and remove the impinger train to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

## 7.2 Sample Recovery.

7.2.1 Discard the contents of the hydrogen peroxide impinger. Carefully rinse the contents of the third, fourth, and fifth impingers into a 500 ml iodine flask.

NOTE: The impingers normally have only a thin film of cadmium sulfide remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow cadmium sulfide remain in the impingers, the alternative recovery procedure described below must be used.

7.2.2 Pipette exactly 50 ml of 0.01 N iodine solution into a 125 ml Erlenmeyer flask. Add 10 ml of 3 M HCl to the solution. Quantitatively rinse the acidified iodine into the iodine flask. Stopper the flask immediately and shake briefly.

7.2.2 (Alternative). Extract the remaining cadmium sulfide from the third, fourth, and fifth impingers using the acidified iodine solution. Immediately after pouring the acidified iodine into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask. Do not transfer any rinse portion from one impinger to another; transfer it directly to the iodine flask. Once the acidified iodine solution has been poured into any glassware containing cadmium sulfide, the container must be tightly stoppered at all times except when adding more solution, and this must be done as quickly and carefully as possible. After adding any acidified iodine solution to the iodine flask, allow a few minutes for absorption of the H<sub>2</sub>S before adding any further rinses. Repeat the iodine extraction until all cadmium sulfide is removed from the impingers. Extract that part of the connecting glassware that contains visible cadmium sulfide.

Quantitatively rinse all of the iodine from the impingers, connectors, and the beaker into the iodine flask using deionized, distilled water. Stopper the flask and shake briefly.

7.2.3 Allow the iodine flask to stand about 30 minutes in the dark for absorption of the H<sub>2</sub>S into the iodine, then complete the titration analysis as in Section 7.3.

NOTE: Caution! Iodine evaporates from acidified iodine solutions. Samples to which acidified iodine have been added may not be stored, but must be analyzed in the time schedule stated in Section 7.2.3.

7.2.4 Prepare a blank by adding 45 ml of cadmium sulfate absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl. Follow the same impinger extracting and quantitative rinsing procedure carried out in sample analysis. Stopper the flask, shake

briefly, let stand 30 minutes in the dark, and titrate with the samples.

NOTE: The blank must be handled by exactly the same procedure as that used for the samples.

### 7.3 Analysis.

NOTE: Titration analyses should be conducted at the sample-cleanup area in order to prevent loss of iodine from the sample. Titration should never be made in direct sunlight.

7.3.1 Using 0.01 N sodium thiosulfate solution (or 0.01 N phenylarsine oxide, if applicable), rapidly titrate each sample in an iodine flask using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V[TT], the volume of sodium thiosulfate solution used, or V[AT], the volume of phenylarsine oxide solution used (ml).

7.3.2 Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

## 8. Calibration and Standards

### 8.1 Standardizations.

8.1.1 Standardize the 0.01 N iodine solution daily as follows: Pipette 25 ml of the iodine solution into a 125 ml Erlenmeyer flask. Add 2 ml of 3 M HCl. Titrate rapidly with standard 0.01 N thiosulfate solution or with 0.01 N phenylarsine oxide until the solution is light yellow, using gentle mixing. Add four drops of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V[T], the volume of thiosulfate solution used, or V[AS], the volume of phenylarsine oxide solution used (ml). Repeat until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml and calculate the exact normality of the iodine solution using Equation 11-3. Repeat the standardization daily.

8.1.2 Standardize the 0.1 N thiosulfate solution as follows: Oven-dry potassium dichromate ( $K_2Cr_2O_7$ ) at 180 to 200 deg. C (360 to 390 deg. F). Weigh to the nearest milligram, 2 g of potassium dichromate. Transfer the dichromate to a 500 ml volumetric flask, dissolve in deionized, distilled water and dilute to exactly 500 ml. In a 500 ml iodine flask, dissolve approximately 3 g of potassium iodide (KI) in 45 ml of deionized, distilled water, then add 10 ml of 3 M hydrochloric acid solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the solution once and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of deionized distilled water, washing down the sides of the flask with part of the water. Titrate with 0.1 N thiosulfate until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V[S], the volume of thiosulfate solution used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using Equation 11-1. Repeat the standardization each week, or after each test series, whichever time is shorter.

8.1.3 Standardize the 0.01 N Phenylarsine oxide (if applicable) as follows: oven dry potassium dichromate ( $K_2Cr_2O_7$ ) at 180 to 200 deg. C (360 to 390 deg. F). Weigh to the nearest milligram, 2 g of the  $K_2Cr_2O_7$ ; transfer the dichromate to a 500 ml volumetric flask, dissolve in deionized, distilled water, and dilute to exactly 500 ml. In a 500 ml iodine flask, dissolve approximately 0.3 g of potassium iodide (KI) in 45 ml of deionized, distilled water; add 10 ml of 3M hydrochloric acid. Pipette 5 ml of the  $K_2Cr_2O_7$  solution into the iodine flask. Gently swirl the contents of the flask once and allow to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of deionized, distilled water, washing down the sides of the flask with part of the water. Titrate with 0.01 N phenylarsine oxide until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V[A], the volume of phenylarsine oxide used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using Equation 11-2. Repeat the standardization each week or after each test series, whichever time is shorter.

8.2 Sampling Train Calibration. Calibrate the sampling train components as follows:

### 8.2.1 Dry Gas Meter.

8.2.1.1 Initial Calibration. The dry gas meter shall be calibrated before its initial use in the field. Proceed as follows: First, assemble the following components in series: Drying tube, needle valve, pump, rotameter, and dry gas meter. Then, leak-check the system as follows: Place a vacuum gauge (at least 760 mm Hg) at the inlet to the drying tube and 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 shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

Next, calibrate the dry gas meter (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 of the drying tube. 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 dry gas meter is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

8.2.1.2 Post-test Calibration Check. After each field test series, conduct a calibration check as in Section 8.2.1.1. 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 8.2.1.1), 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 dry gas meter as in Section 8.2.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

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

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

8.2.4 Barometer. Calibrate against a mercury barometer.

## 9. Calculations

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

9.1 Normality of the Standard (approx. 0.1 N) Thiosulfate Solution.

$$N[S] = 2.039W / V[S]$$

Eq. 11-1

where:

W = Weight of  $K_2Cr_2O_7$  used, g.

V[S] = Volume of  $Na_2S_2O_3$  solution used, ml.

N[S] = Normality of standard thiosulfate solution, g-eq/liter.

2.039 = Conversion factor

(6 eq. I<sub>2</sub>/mole K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) X (1,000 ml/liter) / (294.2 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/mole) X (10 aliquot factor)

9.2 Normality of Standard Phenylarsine Oxide Solution (if applicable).

$N[A] = 0.2039 W / V[A]$

Eq. 11-2

where:

W = Weight of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> used, g.

V[A] = Volume of C<sub>6</sub>H<sub>5</sub>AsO used, ml.

N[A] = Normality of standard phenylarsine oxide solution, g-eq/liter.

0.2039 = Conversion factor

(6 eq. I<sub>2</sub>/mole K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) X (1,000 ml/liter) / (249.2 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/mole) X (100 aliquot factor)

9.3 Normality of Standard Iodine Solution.

$N[I] = N[T] X V[T] / V[I]$

11-3

where:

N[I] = Normality of standard iodine solution, g-eq/liter.

V[I] = Volume of standard iodine solution used, ml.

N[T] = Normality of standard (approx. 0.01 N) thiosulfate solution; assumed to be 0.1 N[S], g-eq/liter.

V[T] = Volume of thiosulfate solution used, ml.

NOTE: If phenylarsine oxide is used instead of thiosulfate, replace N[T] and V[T] in Equation 11-3 with N[A] and V[AS], respectively (see Sections 8.1.1 and 8.1.3).

9.4 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 deg. C and 760 mm Hg.)

$V[m(std)] = V[m] X Y X [(T[std] / T[m]) (P[bar] / P[std])]$

Eq. 11-4

Where:

V[m(std)] = Volume at standard conditions of gas sample through the dry gas meter, standard liters.

V[m] = Volume of gas sample through the dry gas meter (meter conditions), liters.

T[std] = Absolute temperature at standard conditions, 293 deg. K.

T[m] = Average dry gas meter temperature, deg. K.

P[bar] = Barometric pressure at the sampling site, mm Hg.

P[std] = Absolute pressure at standard conditions, 760 mm Hg.

Y = Dry gas meter calibration factor.

9.5 Concentration of H<sub>2</sub>S. Calculate the concentration of H<sub>2</sub>S in the gas stream at standard conditions using the following equation:

$$C[H_2S] = K \times [(V[IT] \times N[I] - V[TT] \times N[T]) \text{ sample} - (V[IT] \times N[I] - V[TT] \times N[T])] / V[m(\text{std})]$$

Eq. 11-5

Where (metric units):

C[H<sub>2</sub>S] = Concentration of H<sub>2</sub>S at standard conditions, mg/dscm.

K = Conversion factor  $17.04 \times 10^3$

$(34.07 \text{ g/mole H}_2\text{S}) \times (1,000 \text{ liters/m}^3) \times (1,000 \text{ mg/g}) / (1,000 \text{ ml/liter}) \times (2\text{H}_2\text{S eq/mole})$

V[IT] = Volume of standard iodine solution = 50.0 ml.

N[I] = Normality of standard iodine solution, g-eq/liter.

V[TT] = Volume of standard (approx. 0.01 N) sodium thiosulfate solution, ml.

N[T] = Normality of standard sodium thiosulfate solution, g-eq/liter.

V[m(std)] = Dry gas volume at standard conditions, liters.

NOTE: If phenylarsine oxide is used instead of thiosulfate, replace N[T] and V[TT] in Equation 11-5 with N[A] and V[AT], respectively (see Sections 7.3.1 and 8.1.3).

## 10. Stability

The absorbing solution is stable for at least 1 month. Sample recovery and analysis should begin within 1 hour of sampling to minimize oxidation of the acidified cadmium sulfide. Once iodine has been added to the sample, the remainder of the analysis procedure must be completed according to Sections 7.2.2 through 7.3.2.

## 11. Bibliography

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## METHOD 12--DETERMINATION OF INORGANIC LEAD EMISSIONS FROM STATIONARY SOURCES

### 1. *Principle and Applicability*

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  $\mu\text{g}$ . 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  $\mu\text{g Pb/ml}$  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<sup>3</sup>.

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 (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 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 deg. C (2 deg. F) at the outlet of the fourth impinger for monitoring purposes.

Figure 12-1. Inorganic lead sampling train.

[SEE FIGURE IN ORIGINAL]

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 N nitric acid (HNO<sub>3</sub>) 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<sub>3</sub>. (Narrow mouth glass bottles have been found to be less prone to leakage.)

\* Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

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 >SO>.

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, Sections 3.1.2, 3.1.4, and 3.1.5, respectively.

4.1.3 Water. Deionized distilled, to conform to ASTM Specification D1192-77 (incorporated by reference--see § 60.17), Type 3. If high concentrations of organic matter 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<sub>3</sub> 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<sub>3</sub> is needed. Dilute 390 ml of concentrated HNO<sub>3</sub> to 1 liter with deionized distilled water.

4.3 Sample Recovery. 0.1 N HNO<sub>3</sub> (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<sub>3</sub> 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<sub>3</sub>)<sub>2</sub>] in about 60 ml of deionized distilled water, add 2 ml concentrated HNO<sub>3</sub>, 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<sub>3</sub> 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<sub>2</sub>O<sub>2</sub> 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 N HNO<sub>3</sub> 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 sampling 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<sub>3</sub> 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<sub>3</sub> used for each rinse. Perform the 0.1 N HNO<sub>3</sub> rinses as follows:

Carefully remove the probe nozzle and rinse the inside surfaces with 0.1 N HNO<sub>3</sub> from a wash bottle while brushing with a stainless steel, Nylon-bristle brush. Brush until the 0.1 N HNO<sub>3</sub> rinse shows no visible particles, then make a final rinse of the inside surface.

Brush and rinse with 0.1 N HNO<sub>3</sub> 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<sub>3</sub>. While rotating the probe so that all inside surfaces will be rinsed with 0.1 N HNO<sub>3</sub>, tilt the probe and squirt 0.1 N HNO<sub>3</sub> into its upper end. Let the 0.1 N HNO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> the inside of the front half of the filter holder. Brush and rinse each surface 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<sub>3</sub> 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<sub>3</sub> used for rinsing. Pour approximately 30 ml of 0.1 N HNO<sub>3</sub> into each of the first three impingers and agitate the impingers. Drain the 0.1 N HNO<sub>3</sub> 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<sub>3</sub>; 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> for every 100 mg of sample collected in the train or a minimum of 30 ml of 50 percent HNO<sub>3</sub> 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<sub>3</sub>. Add 10 ml of 3 percent H<sub>2</sub>O<sub>2</sub> and continue heating for 10 min. Add 50 ml of hot (80 deg. 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<sub>3</sub> and treat as described in Section 5.3.3 using 10 ml of 3 percent H<sub>2</sub>O<sub>2</sub> and 50 ml of hot, deionized distilled water. Filter and dilute to a total volume of 100 ml using deionized distilled water.

5.3.5 *0.1 N HNO<sub>3</sub> Blank*. Take the entire 200 ml of 0.1 N HNO<sub>3</sub> to dryness on a steam bath, add 15 ml of 50 percent HNO<sub>3</sub>, and treat as described in Section 5.3.3 using 10 ml of 3 percent H<sub>2</sub>O<sub>2</sub> 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<sub>3</sub> 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 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  $\mu\text{g/ml}$  of the sample solution by using the following equation:

$$C[s] = C[a] \frac{A[s]}{A[t] - A[s]}$$

Eq. 12-1

Where:

C[a] = Pb concentration of the standard solution,  $\mu\text{g/ml}$ .

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 Pb 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 Citation 1 of Bibliography) may also be used. In any event, if the results of the method of additions procedure used on the single 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.

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  $\mu\text{g Pb/ml}$  (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  $V[m(\text{std})]$ , the total volume of dry gas metered corrected to standard conditions (20 deg. C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust  $V[w(\text{std})]$  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  $V[w(\text{std})]$  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  $\text{HNO}_3$  blank. Use the calibration curve and this corrected absorbance to determine the  $\mu\text{g Pb}$  concentration in the sample aspirated into the spectrophotometer. Calculate the total Pb content  $C \text{ deg. [Pb]}$  (in  $\mu\text{g}$ ) 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  $C[\text{Pb}]$  in  $\text{mg/dscm}$  as follows:

$$C[\text{Pb}] = K \times C \text{ deg. [Pb]} / V[m(\text{std})]$$

Eq. 12-2

Where:

$K = 0.001 \text{ mg}/\mu\text{g}$  for metric units.

$= 2.205 \text{ lb}/\mu\text{g} \times 10^{-9}$  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  $\text{HNO}_3$  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<sub>3</sub>, 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*

1. Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, CT. September 1976.
2. American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. Philadelphia, PA. 1974. p. 40-42.
3. Klein, R. and C. Hach. Standard Additions -- Uses and Limitations in Spectrophotometric Analysis. *Amer. Lab.* 9:21-27. 1977.
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, NC. (Presented at National APCA Meeting. Houston. June 26, 1978).
5. Same as Method 5, Citations 2 to 5 and 7 of bibliography.

## METHOD 13A -- DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES; SPADNS ZIRCONIUM LAKE METHOD

### 1. *Principle and Applicability*

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from 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 SPADNS Zirconium Lake Colorimetric Method.

### 2. *Range and Sensitivity*

The range of this method is 0 to 1.4  $\mu\text{g F/ml}$ . Sensitivity has not been determined.

### 3. *Interferences*

Large quantities of chloride will interfere with the analysis, but this interference can be prevented by adding silver sulfate into the distillation flask (see Section 7.3.4). If chloride ion is present, it may be easier to use the Specific Ion Electrode Method (Method 13B). Grease on sample-exposed surfaces may cause low F results due to adsorption.

### 4. *Precision, Accuracy, and Stability*

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 total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F/m<sup>3</sup>. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, were 0.044 mg F/m<sup>3</sup> with 60 degrees of freedom and 0.064 mg F/m<sup>3</sup> with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

4.3 Stability. After the sample and colorimetric reagent are mixed, the color formed is stable for approximately 2 hours. A 3 deg. C temperature difference between the sample and standard solutions produces an error of approximately 0.005 mg F/liter. To avoid this error, the absorbances of the sample and standard solutions must be measured at the same temperature.

## 5. Apparatus

5.1 Sampling Train. A schematic of the sampling train is shown in Figure 13A-1; it is similar to the Method 5 train except the filter position is interchangeable. The sampling train consists of the following components:

5.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.6, 2.1.8, 2.1.9, and 2.1.10. When moisture condensation is a problem, the filter heating system is used.

5.1.2 Probe Liner. Borosilicate glass or 316 stainless steel. When the filter is located immediately after the probe, the tester may use a probe heating system to prevent filter plugging resulting from moisture condensation, but the tester shall not allow the temperature in the probe to exceed 120 +/- 14 deg. C (248 +/- 25 deg. F).

5.1.3 Filter Holder. With positive seal against leakage from the outside or around the filter. If the filter is located between the probe and first impinger, use borosilicate glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket; do not use a glass frit or a sintered metal filter support. If the filter is located between the third and fourth impingers, the tester may use borosilicate glass with a glass frit filter support and a silicone rubber gasket. The tester may also use other materials of construction with approval from the Administrator.

5.1.4 Impingers. Four impingers connected as shown in Figure 13A-1 with ground-glass (or equivalent), vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm-inside-diameter (1/2 in.) glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. The tester may use modifications (e.g., flexible connections between the impingers or materials other than glass), subject to the approval of the Administrator. Place a thermometer, capable of measuring temperature to within 1 deg. C (2 deg. F), at the outlet of the fourth impinger for monitoring purposes.

5.2 Sample Recovery. The following items are needed:

5.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Graduated Cylinder and/or Balance, Plastic Storage Containers, Rubber Policeman, Funnel. Same as Method 5, Sections 2.2.1 to 2.2.2 and 2.2.5 to 2.2.8, respectively.

5.2.2 Sample Storage Container. Widemouth, high-density-polyethylene bottles for impinger water samples, 1-liter.

5.3 Analysis. The following equipment is needed:

5.3.1 Distillation Apparatus. Glass distillation apparatus assembled as shown in Figure 13A-2.

5.3.2 Bunsen Burner.

5.3.3 Electric Muffle Furnace. Capable of heating to 600 deg. C.

5.3.4 Crucibles. Nickel, 75- to 100-ml.

5.3.5 Beakers. 500-ml and 1500-ml.

5.3.6 Volumetric Flasks. 50-ml.

5.3.7 Erlenmeyer Flasks or Plastic Bottles. 500-ml.

5.3.8 Constant Temperature Bath. Capable of maintaining a constant temperature of +/- 1.0 deg. C at room temperature conditions.

5.3.9 Balance. 300-g capacity to measure to +/- 0.5 g.

5.3.10 Spectrophotometer. Instrument that measures absorbance at 570 nm and provides at least a 1-cm light path.

5.3.11 Spectrophotometer Cells. 1-cm pathlength.

## 6. Reagents

6.1 Sampling. Use ACS reagent-grade chemicals or equivalent, unless otherwise specified. The reagents used in sampling are as follows:

### 6.1.1 Filters.

6.1.1.1 If the filter is located between the third and fourth impingers, use a Whatman n1 No. 1 filter, or equivalent, sized to fit the filter holder.

n1 Mention of company or product names does not constitute endorsement by the U.S. Environmental Protection Agency.

[SEE FIGURE IN ORIGINAL]

Figure 13A-1. Fluoride sampling train.

[SEE FIGURE IN ORIGINAL]

Figure 13A-2. Fluoride distillation apparatus.

6.1.1.2 If the filter is located between the probe and first impinger, use any suitable medium (e.g., paper, organic membrane) that conforms to the following specifications: (1) The filter can withstand prolonged exposure to temperatures up to 135 deg. C (275 deg. F). (2) The filter has at least 95 percent collection efficiency ( $\leq 5$  percent penetration) for 0.3  $\mu$ m dioctyl phthalate smoke particles. Conduct the filter efficiency test before the test series, using ASTM Standard Method D 2986-71, or use test data from the supplier's quality control program. (3) The filter has a low F blank value ( $\leq 0.015$  mg F/cm<sup>2</sup> of filter area). Before the test series, determine the average F blank value of at least three filters (from the lot to be used for sampling) using the applicable procedures described in Sections 7.3 and 7.4 of this method. In general, glass fiber filters have high and/or variable F blank values, and will not be acceptable for use.

6.1.2 Water. Deionized distilled, to conform to ASTM Specification D 1193-74, Type 3. If high concentrations

of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter.

6.1.3 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, Sections 3.1.2, 3.1.4, and 3.1.5, respectively.

6.2 Sample Recovery. Water, from same container as described in Section 6.1.2, is needed for sample recovery.

6.3 Sample Preparation and Analysis. The reagents needed for sample preparation and analysis are as follows:

6.3.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.3.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of deionized distilled water.

6.3.3 Silver Sulfate (Ag<sub>2</sub>SO<sub>4</sub>).

6.3.4 Sodium Hydroxide (NaOH). Pellets.

6.3.5 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), Concentrated.

6.3.6 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H<sub>2</sub>SO<sub>4</sub> with 3 parts of deionized distilled water.

6.3.7 Filters. Whatman No. 541, or equivalent.

6.3.8 Hydrochloric Acid (HCl), Concentrated.

6.3.9 Water. From same container as described in Section 6.1.2.

6.3.10 Fluoride Standard Solution, 0.01 mg F/ml. Dry in an oven at 110 deg. C for at least 2 hours. Dissolve 0.2210 g of NaF in 1 liter of deionized distilled water. Dilute 100 ml of this solution to 1 liter with deionized distilled water.

6.3.11 SPADNS Solution [4, 5 dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene-disulfonic acid trisodium salt]. Dissolve 0.960 +/- 0.010 g of SPADNS reagent in 500 ml deionized distilled water. If stored in a well-sealed bottle protected from the sunlight, this solution is stable for at least 1 month.

6.3.12 Spectrophotometer Zero Reference Solution. Prepare daily. Add 10 ml of SPADNS solution (6.3.11) to 100 ml deionized distilled water, and acidify with a solution prepared by diluting 7 ml of concentrated HCl to 10 ml with deionized distilled water.

6.3.13 SPADNS Mixed Reagent. Dissolve 0.135 +/- 0.005 g of zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) in 25 ml of deionized distilled water. Add 350 ml of concentrated HCl, and dilute to 500 ml with deionized distilled water. Mix equal volumes of this solution and SPADNS solution to form a single reagent. This reagent is stable for at least 2 months.

## 7. Procedure

7.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedures to assure reliable results.

7.1.1 Pretest Preparation. Follow the general procedure given in Method 5, Section 4.1.1, except the filter need not be weighed.

7.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, Section 4.1.2., except the nozzle size selected must maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

7.1.3 Preparation of Collection Train. Follow the general procedure given in Method 5, Section 4.1.3, except for the following variations:

Place 100 ml of deionized distilled water in each of the first two impingers, and leave the third impinger empty. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger.

Assemble the train as shown in Figure 13A-1 with the filter between the third and fourth impingers. Alternatively, if a 20-mesh stainless steel screen is used for the filter support, the tester may place the filter between the probe and first impinger. The tester may also use a filter heating system to prevent moisture condensation, but shall not allow the temperature around the filter holder to exceed 120 +/- 14 deg. C (248 +/- 25 deg. F). Record the filter location on the data sheet.

7.1.4 Leak-Check Procedures. Follow the 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).

7.1.5 Fluoride Train Operation. Follow the general procedure given in Method 5, Section 4.1.5, keeping the filter and probe temperatures (if applicable) at 120 +/- 14 deg. C (248 +/- 25 deg. F) and isokinetic sampling rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-2.

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 all external particulate matter near the tip of the probe nozzle and place a cap over it to keep from losing part of the sample. Do not cap off the probe tip tightly while the sampling train is cooling down, because a vacuum would form in the filter holder, thus drawing impinger water backwards.

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, if present. Remove the filter assembly, wipe off the silicone grease from the filter holder inlet, and cap this inlet. Remove the umbilical cord from the last impinger, and cap the impinger. After wiping off the silicone grease, cap off the filter holder outlet and any open impinger inlets and outlets. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to an area that is clean and protected from the wind so that the chances of contaminating or losing the sample is minimized.

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

7.2.1 *Container No. 1* (Probe, Filter, and Impinger Catches). Using a graduated cylinder, measure to the nearest ml, and record the volume of the water in the first three impingers; include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into this polyethylene container. Add the filter to this container. (The filter may be handled separately using procedures subject to the Administrator's approval.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the

sample, clean all sample-exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) with deionized distilled water. Use less than 500 ml for the entire wash. Add the washings to the sampler container. Perform the deionized distilled water rinses as follows:

Carefully remove the probe nozzle and rinse the inside surface with deionized distilled water from a wash bottle. Brush with a Nylon bristle brush, and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with deionized distilled water in a similar way.

Rinse the probe liner with deionized distilled water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt deionized distilled water into the upper end 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 water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. 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 deionized distilled water, 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 sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Rinse the inside surface of each of the first three impingers (and connecting glassware) three separate times. Use a small portion of deionized distilled water for each rinse, and brush each sample-exposed surface with a Nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with deionized distilled water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface three times or more if needed. Make a final rinse of the brush and filter holder.

After all water washings and particulate matter have been collected in the sample container, tighten the lid so that water 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 clearly to identify its contents.

*7.2.2 Container No. 2 (Sample Blank).* Prepare a blank by placing an unused filter in a polyethylene container and adding a volume of water equal to the total volume in Container No. 1. Process the blank in the same manner as for Container No. 1.

*7.2.3 Container No. 3 (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 the fourth impinger to its 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 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, the tester may follow the analytical procedure for Container No. 3 in Section 7.4.2.

*7.3 Sample Preparation and Distillation.* (Note the liquid levels in Containers No. 1 and No. 2 and confirm on the analysis sheet whether or not leakage occurred during transport. If noticeable leakage had occurred, either

void the sample or use methods, subject to the approval of the Administrator, to correct the final results.) Treat the contents of each sample container as described below:

7.3.1 *Container No. 1* (Probe, Filter, and Impinger Catches). Filter this container's contents, including the sampling filter, through Whatman No. 541 filter paper, or equivalent, into a 1500-ml beaker.

7.3.1.1 If the filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH, and evaporate to less than 900 ml.

7.3.1.2 Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of deionized distilled water, and macerate the filters with a glass rod.

Add 100 mg CaO to the crucible, and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible in a hood under infrared lamps or on a hot plate at low heat. Evaporate the water completely. During the evaporation of the water, keep the slurry basic (red to phenolphthalein) to avoid loss of F. If the indicator turns colorless (acidic) during the evaporation, add CaO until the color turns red again.

After evaporation of the water, place the crucible on a hot plate under a hood and slowly increase the temperature until the Whatman No. 541 and sampling filters char. It may take several hours to completely char the filters.

Place the crucible in a cold muffle furnace. Gradually (to prevent smoking) increase the temperature to 600 deg. C, and maintain until the contents are reduced to an ash. Remove the crucible from the furnace and allow to cool.

Add approximately 4 g of crushed NaOH to the crucible and mix. Return the crucible to the muffle furnace, and fuse the sample for 10 minutes at 600 deg. C.

Remove the sample from the furnace, and cool to ambient temperature. Using several rinsings of warm deionized distilled water, transfer the contents of the crucible to the beaker containing the filtrate. To assure complete sample removal, rinse finally with two 20-ml portions of 25 percent H<sub>2</sub>SO<sub>4</sub>, and carefully add to the beaker. Mix well, and transfer to a 1-liter volumetric flask. Dilute to volume with deionized distilled water, and mix thoroughly. Allow any undissolved solids to settle.

7.3.2 *Container No. 2* (Sample Blank). Treat in the same manner as described in Section 7.3.1 above.

7.3.3 Adjustment of Acid/Water Ratio in Distillation Flask. (Use a protective shield when carrying out this procedure.) Place 400 ml of deionized distilled water in the distillation flask, and add 200 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. (Caution: Observe standard precautions when mixing H<sub>2</sub>SO<sub>4</sub> with water. Slowly add the acid to the flask with constant swirling.) Add some soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 13A-2. Heat the flask until it reaches a temperature of 175 deg. C to adjust the acid/water ratio for subsequent distillations. Discard the distillate.

7.3.4 Distillation. Cool the contents of the distillation flask to below 80 deg. C. Pipet an aliquot of sample containing less than 10.0 mg F directly into the distillation flask, and add deionized distilled water to make a total volume of 220 ml added to the distillation flask. (To estimate the appropriate aliquot size, select an aliquot of the solution and treat as described in Section 7.4.1. This will be an approximation of the F content because of possible interfering ions.)

Note: If the sample contains chloride, add 5 mg of Ag<sub>2</sub>SO<sub>4</sub> to the flask for every mg of chloride.

Place a 250-ml volumetric flask at the condenser exit. Heat the flask as rapidly as possible with a Bunsen burner, and collect all the distillate up to 175 deg. C. During heatup, play the burner flame up and down the side of the flask to prevent bumping. Conduct the distillation as rapidly as possible (15 minutes or less). Slow distillations have been found to produce low F recoveries. Caution: Be careful not to exceed 175 deg. C to avoid causing H<sub>2</sub>SO<sub>4</sub> to distill over.

If F distillation in the mg range is to be followed by a distillation in the fractional mg range, add 220 ml of deionized distilled water and distill it over as in the acid adjustment step to remove residual F from the distillation system.

The tester may use the acid in the distillation flask until there is carry-over of interferences or poor F recovery. Check for these every tenth distillation using a deionized distilled water blank and a standard solution. Change the acid whenever the F recovery is less than 90 percent or the blank value exceeds 0.1 mu g/ml.

#### 7.4 Analysis.

7.4.1 Containers No. 1 and No. 2. After distilling suitable aliquots from Containers No. 1 and No. 2 according to Section 7.3.4, dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water, and mix thoroughly. Pipet a suitable aliquot of each sample distillate (containing 10 to 40 mu g F/ml) into a beaker, and dilute to 50 ml with deionized distilled water. Use the same aliquot size for the blank. Add 10 ml of SPADNS mixed reagent (6.3.13), and mix thoroughly.

After mixing, place the sample in a constant-temperature bath containing the standard solutions (see Section 8.2) for 30 minutes before reading the absorbance on the spectrophotometer.

Set the spectrophotometer to zero absorbance at 570 nm with the reference solution (6.3.12), and check the spectrophotometer calibration with the standard solution. Determine the absorbance of the samples, and determine the concentration from the calibration curve. If the concentration does not fall within the range of the calibration curve, repeat the procedure using a different size aliquot.

7.4.2 *Container No. 3* (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. The tester may conduct this step in the field.

### 8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Calibrate the sampling train components according to the indicated sections in 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 Metering System (Section 5.6); and Barometer (Section 5.7).

8.2 Spectrophotometer. Prepare the blank standard by adding 10 ml of SPADNS mixed reagent to 50 ml of deionized distilled water. Accurately prepare a series of standards from the 0.01 mg F/ml standard fluoride solution (6.3.10) by diluting 0, 2, 4, 6, 8, 10, 12, and 14 ml to 100 ml with deionized distilled water. Pipet 50 ml from each solution and transfer each to a separate 100-ml beaker. Then add 10 ml of SPADNS mixed reagent to each. These standards will contain 0, 10, 20, 30, 40, 50, 60, and 70 mu g F (0 to 1.4 mu g/ml), respectively.

After mixing, place the reference standards and reference solution in a constant temperature bath for 30 minutes before reading the absorbance with the spectrophotometer. Adjust all samples to this same temperature before analyzing.

With the spectrophotometer at 570 nm, use the reference solution (6.3.12) to set the absorbance to zero.

Determine the absorbance of the standards. Prepare a calibration curve by plotting  $\mu\text{g F}/50\text{ ml}$  versus absorbance on linear graph paper. Prepare the standard curve initially and thereafter whenever the SPADNS mixed reagent is newly made. Also, run a calibration standard with each set of samples and if it differs from the calibration curve by  $\pm 2$  percent, prepare a new standard curve.

## 9. Calculations

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

### 9.1 Nomenclature

$A[d]$  = Aliquot of distillate taken for color development, ml.

$A[t]$  = Aliquot of total sample added to still, ml.

$B[ws]$  = Water vapor in the gas stream, proportion by volume.

$C[s]$  = Concentration of F in stack gas,  $\text{mg}/\text{m}^3$  ( $\text{mg}/\text{ft}^3$ ), dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293 deg. K (528 deg. R).

$F[t]$  = Total F in sample, mg.

$\mu\text{g F}$  = Concentration from the calibration curve,  $\mu\text{g}$ .

$T[m]$  = Absolute average dry gas meter temperature (see Figure 5-2 of Method 5), deg. K (deg. R).

$T[s]$  = Absolute average stack gas temperature (see Figure 5-2 of Method 5), deg. K (deg. R).

$V[d]$  = Volume of distillate as diluted, ml.

$V[m(\text{std})]$  = Volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf).

$V[t]$  = Total volume of F sample, after final dilution, ml.

$V[w(\text{std})]$  = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5-2 of Method 5).

9.3 Dry Gas Volume, Calculate  $V[m(\text{std})]$  and adjust for leakage, if necessary, using the equation in Section 6.3 of Method 5.

9.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor  $V[w(\text{std})]$  and moisture content  $B[ws]$  from the data obtained in this method (Figure 13A-1); use Equations 5-2 and 5-3 of Method 5.

9.5 Concentration.

9.5.1 Total Fluoride in Sample. Calculate the amount of F in the sample using the following equation:

$$F[t] = 10^{-3} \times (V[t] / A[t]) \times (V[d] / A[d]) \times (\mu\text{g F})$$

Eq. 13A-1

9.5.2 Fluoride Concentration in Stack Gas. Determine the F concentration in the stack gas using the following equation:

$$C[s] = F[t] / V[m(\text{std})]$$

Eq. 13A-2

9.6 Isokinetic Variation and Acceptable Results. Use Method 5, Sections 6.11 and 6.12.

## 10. Bibliography

1. Bellack, Ervin, Simplified Fluoride Distillation Method. Journal of the American Water Works Association. 50:5306. 1958.
2. Mitchell, W. J., J. C. Suggs, and F. J. Bergman. Collaborative Study of EPA Method 13A and Method 13B. Publication No. EPA-600/4-77-050. Environmental Protection Agency. Research Triangle Park, NC. December 1977.
3. Mitchell, W. J. and M. R. Midgett. Adequacy of Sampling Trains and Analytical Procedures Used for Fluoride. *Atm. Environ.* 10:865-872. 1976.

## METHOD 13B -- DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES -- SPECIFIC ION ELECTRODE METHOD

### 1. Principle and Applicability

- 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  $\mu\text{g F/ml}$ ; however, measurements of less than 0.1  $\mu\text{g F/ml}$  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 total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4  $\text{mg F/m}^3$ . The within-laboratory and between-laboratory standard deviations, which include sampling and

analysis errors, are 0.037 mg F/m<sup>3</sup> with 60 degrees of freedom and 0.056 mg F/m<sup>3</sup> 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 n<sub>2</sub> Fluorocarbon-Coated Stirring Bars.

n<sub>2</sub> Mention of any trade name or specific product does not constitute endorsement by the U.S. Environmental Protection Agency.

## 6. Reagents

6.1 Sampling and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Analysis. Use ACS reagent grade chemicals (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<sub>2</sub>SO<sub>4</sub>), 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<sub>2</sub>SO<sub>4</sub> 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 deg. 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 deg. 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, Sections 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:

$$F[t] = K \times (V[t] / A[t]) \times V[d] \times M$$

Eq. 13B-1

Where:

K = 19 mg/millimole.

## 10. Bibliography

1. Same as Method 13A, Citations 1 and 2 of Bibliography.

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 14 -- DETERMINATION OF FLUORIDE EMISSIONS FROM POTROOM ROOF MONITORS FOR PRIMARY ALUMINUM PLANTS

### 1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of fluoride emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards.

1.2 Principle. Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The gas in the duct is sampled using Method 13A or 13B -- Determination of Total Fluoride Emissions from Stationary Sources. Effluent velocity and volumetric flow rate are determined with anemometers located in the roof monitor.

## 2. Apparatus

### 2.1 Velocity Measurement Apparatus.

2.1.1 Anemometers. Propeller anemometers, or equivalent. Each anemometer shall meet the following specifications: (1) Its propeller shall be made of polystyrene, or similar material of uniform density. To insure uniformity of performance among propellers, it is desirable that all propellers be made from the same mold; (2) The propeller shall be properly balanced, to optimize performance; (3) When the anemometer is mounted horizontally, its threshold velocity shall not exceed 15 m/min (50 fpm); (4) The measurement range of the anemometer shall extend to at least 600 m/min (2,000 fpm); (5) The anemometer shall be able to withstand prolonged exposure to dusty and corrosive environments; one way of achieving this is to continuously purge the bearings of the anemometer with filtered air during operation; (6) All anemometer components shall be properly shielded or encased, such that the performance of the anemometer is uninfluenced by potroom magnetic field effects; (7) A known relationship shall exist between the electrical output signal from the anemometer generator and the propeller shaft rpm, at a minimum of three evenly spaced rpm settings between 60 and 1800 rpm; for the 3 settings, use 60 +/- 15, 900 +/- 100, and 1800 +/- 100 rpm. Anemometers having other types of output signals (e.g., optical) may be used, subject to the approval of the Administrator. If other types of anemometers are used, there must be a known relationship (as described above) between output signal and shaft rpm; also, each anemometer must be equipped with a suitable readout system (See Section 2.1.3).

#### 2.1.2 Installation of Anemometers.

2.1.2.1 If the affected facility consists of a single, isolated potroom (or potroom segment), install at least one anemometer for every 85 m of roof monitor length. If the length of the roof monitor divided by 85 m is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. For monitors that are less than 130 m in length, use at least two anemometers. Divide the monitor cross-section into as many equal areas as anemometers and locate an anemometer at the centroid of each equal area. See exception in Section 2.1.2.3.

2.1.2.2 If the affected facility consists of two or more potrooms (or potroom segments) ducted to a common control device, install anemometers in each potroom (or segment) that contains a sampling manifold. Install at least one anemometer for every 85 m of roof monitor length of the potroom (or segment). If the potroom (or segment) length divided by 85 is not a whole number, round the fraction to the nearest whole number to determine the number of anemometers needed. If the potroom (or segment) length is less than 130 m, use at least two anemometers. Divide the potroom (or segment) monitor cross-section into as many equal areas as anemometers and locate an anemometer at the centroid of each equal area. See exception in Section 2.1.2.3.

2.1.2.3 At least one anemometer shall be installed in the immediate vicinity (i.e., within 10 m) of the center of the manifold (See Section 2.2.1). For its placement in relation to the width of the monitor, there are two alternatives. The first is to make a velocity traverse of the width of the roof monitor where an anemometer is to be placed and install the anemometer at a point of average velocity along this traverse. The traverse may be made with any suitable low velocity measuring device, and shall be made during normal process operating conditions.

The second alternative, at the option of the tester, is to install the anemometer halfway across the width of the roof monitor. In this latter case, the velocity traverse need not be conducted.

2.1.3 Recorders. Recorders, equipped with suitable auxiliary equipment (e.g. transducers) for converting the output signal from each anemometer to a continuous recording of air flow velocity, or to an integrated measure of volumetric flowrate. A suitable recorder is one that allows the output signal from the propeller anemometer to be read to within 1 percent when the velocity is between 100 and 120 m/min (350 and 400 fpm). For the purpose of recording velocity, "continuous" shall mean one readout per 15-minute or shorter time interval. A constant amount of time shall elapse between readings. Volumetric flow rate may be determined by an electrical count of anemometer revolutions. The recorders or counters shall permit identification of the velocities or flowrate measured by each individual anemometer.

2.1.4 Pitot Tube. Standard-type pitot tube, as described in Section 2.7 of Method 2, and having a coefficient of 0.99 +/- 0.01.

2.1.5 Pitot Tube (Optional). Isolated, Type S pitot, as described in Section 2.1 of Method 2. The pitot tube shall have a known coefficient, determined as outlined in Section 4.1 of Method 2.

2.1.6 Differential Pressure Gauge. Inclined manometer or equivalent, as described in Section 2.1.2 of Method 2.

## 2.2 Roof Monitor Air Sampling System.

2.2.1 Sampling Ductwork. A minimum of one manifold system shall be installed for each potroom group (as defined in Subpart S, Section 60.191). The manifold system and connecting duct shall be permanently installed to draw an air sample from the roof monitor to ground level. A typical installation of a duct for drawing a sample from a roof monitor to ground level is shown in Figure 14-1. A plan of a manifold system that is located in a roof monitor is shown in Figure 14.2. These drawings represent a typical installation for a generalized roof monitor. The dimensions on these figures may be altered slightly to make the manifold system fit into a particular roof monitor, but the general configuration shall be followed. There shall be eight nozzles, each having a diameter of 0.40 to 0.50 m. Unless otherwise specified by the Administrator, the length of the manifold system from the first nozzle to the eighth shall be 35 m or eight percent of the length of the potroom (or potroom segment) roof monitor, whichever is greater. The duct leading from the roof monitor manifold shall be round with a diameter of 0.30 to 0.40 m. As shown in Figure 14-2, each of the sample legs of the manifold shall have a device, such as a blast gate or valve, to enable adjustment of the flow into each sample nozzle.

Figure 14-1. Roof monitor sampling system.

[SEE FIGURE IN ORIGINAL]

[SEE FIGURE IN ORIGINAL]

Figure 14-2. Sampling manifold and nozzles.

The manifold shall be located in the immediate vicinity of one of the propeller anemometers (see Section 2.1.2.3) and as close as possible to the midsection of the potroom (or potroom segment). Avoid locating the manifold near the end of a potroom or in a section where the aluminum reduction pot arrangement is not typical of the rest of the potroom (or potroom segment). Center the sample nozzles in the throat of the roof monitor (see Figure 14-1). Construct all sample-exposed surfaces within the nozzles, manifold and sample duct of 316 stainless steel. Aluminum may be used if a new ductwork system is conditioned with fluoride-laden roof monitor air for a period of six weeks prior to initial testing. Other materials of construction may be used if it is demonstrated through comparative testing that there is no loss of fluorides in the system. All connections in the

ductwork shall be leak free.

Locate two sample ports in a vertical section of the duct between the roof monitor and exhaust fan. The sample ports shall be at least 10 duct diameters downstream and three diameters upstream from any flow disturbance such as a bend or contraction. The two sample ports shall be situated 90 deg. apart. One of the sample ports shall be situated so that the duct can be traversed in the plane of the nearest upstream duct bend.

2.2.2 Exhaust Fan. An industrial fan or blower shall be attached to the sample duct at ground level (see Figure 14-1). This exhaust fan shall have a capacity such that a large enough volume of air can be pulled through the ductwork to maintain an isokinetic sampling rate in all the sample nozzles for all flow rates normally encountered in the roof monitor.

The exhaust fan volumetric flow rate shall be adjustable so that the roof monitor air can be drawn isokinetically into the sample nozzles. This control of flow may be achieved by a damper on the inlet to the exhauster or by any other workable method.

### 2.3 Temperature Measurement Apparatus.

2.3.1 Thermocouple. Install a thermocouple in the roof monitor near the sample duct. The thermocouple shall conform to the specifications outlined in Section 2.3 of Method 2.

2.3.2 Signal Transducer. Transducer, to change the thermocouple voltage output to a temperature readout.

2.3.3 Thermocouple Wire. To reach from roof monitor to signal transducer and recorder.

2.3.4 Recorder. Suitable recorder to monitor the output from the thermocouple signal transducer.

2.4 Fluoride Sampling Train. Use the train described in Method 13A or 13B.

## 3. Reagents

3.1 Sampling and Analysis. Use reagents described in Method 13A or 13B.

## 4. Calibration

4.1 Initial Performance Checks. Conduct these checks within 60 days prior to the first performance test.

4.1.1 Propeller Anemometers. Anemometers which meet the specifications outlined in Section 2.1.1 need not be calibrated, provided that a reference performance curve relating anemometer signal output to air velocity (covering the velocity range of interest) is available from the manufacturer. For the purpose of this method, a "reference" performance curve is defined as one that has been derived from primary standard calibration data, with the anemometer mounted vertically. "Primary standard" data are obtainable by: (1) Direct calibration of one or more of the anemometers by the National Bureau of Standards (NBS); (2) NBS-traceable calibration; or (3) Calibration by direct measurement of fundamental parameters such as length and time (e.g., by moving the anemometers through still air at measured rates of speed, and recording the output signals). If a reference performance curve is not available from the manufacturer, such a curve shall be generated, using one of the three methods described as above. Conduct a performance-check as outlined in Sections 4.1.1.1 through 4.1.1.3, below. Alternatively, the tester may use any other suitable method, subject to the approval of the Administrator, that takes into account the signal output, propeller condition and threshold velocity of the anemometer.

4.1.1.1 Check the signal output of the anemometer by using an accurate rpm generator (see Figure 14-3) or synchronous motors to spin the propeller shaft at each of the three rpm settings described in Section 2.1.1 above

(specification No. 7), and measuring the output signal at each setting. If, at each setting, the output signal is within +/- 5 percent of the manufacturer's value, the anemometer can be used. If the anemometer performance is unsatisfactory, the anemometer shall either be replaced or repaired.

4.1.1.2 Check the propeller condition, by visually inspecting the propeller, making note of any significant damage or warpage; damaged or deformed propellers shall be replaced.

4.1.1.3 Check the anemometer threshold velocity as follows: With the anemometer mounted as shown in Figure 14-4(A), fasten a known weight (a straight-pin will suffice) to the anemometer propeller at a fixed distance from the center of the propeller shaft. This will generate a known torque; for example, a 0.1 g weight, placed 10 cm from the center of the shaft, will generate a torque of 1.0 g-cm. If the known torque causes the propeller to rotate downward, approximately 90 deg. [see Figure 14-4(B)], then the known torque is greater than or equal to the starting torque; if the propeller fails to rotate approximately 90 deg., the known torque is less than the starting torque. By trying different combinations of weight and distance, the starting torque of a particular anemometer can be satisfactorily estimated. Once an estimate of the starting torque has been obtained, the threshold velocity of the anemometer (for horizontal mounting) can be estimated from a graph such as Figure 14-5 (obtained from the manufacturer). If the horizontal threshold velocity is acceptable [ $<15$  m/min (50 fpm), when this technique is used], the anemometer can be used. If the threshold velocity of an anemometer is found to be unacceptably high, the anemometer shall either be replaced or repaired.

Figure 14-3. Typical RPM generator.

[SEE FIGURE IN ORIGINAL]

Figure 14-4. Check of anemometer starting torque. A "y" gram weight placed "x" centimeters from center of propeller shaft produces a torque of "xy" g-cm. The minimum torque which produces a 90 deg. (approximately) rotation of the propeller is the "starting torque."

[SEE FIGURE IN ORIGINAL]

[SEE FIGURE IN ORIGINAL]

Figure 14-5. Typical curve of starting torque vs horizontal threshold velocity for propeller anemometers. Based on data obtained by R. M. Young Company, May, 1977.

4.1.2 Thermocouple. Check the calibration of the thermocouple-potentiometer system, using the procedures outlined in Section 4.3 of Method 2, at temperatures of 0, 100, and 150 deg. C. If the calibration is off by more than 5 deg. C at any of the temperatures, repair or replace the system; otherwise, the system can be used.

4.1.3 Recorders and/or Counters. Check the calibration of each recorder and/or counter (see Section 2.1.3) at a minimum of three points, approximately spanning the expected range of velocities. Use the calibration procedures recommended by the manufacturer, or other suitable procedures (subject to the approval of the Administrator). If a recorder or counter is found to be out of calibration, by an average amount greater than 5 percent for the three calibration points, replace or repair the system; otherwise, the system can be used.

4.1.4 Manifold Intake Nozzles. In order to balance the flow rates in the eight individual nozzles, proceed as follows: Adjust the exhaust fan to draw a volumetric flow rate (refer to Equation 14-1) such that the entrance velocity into each manifold nozzle approximates the average effluent velocity in the roof monitor. Measure the velocity of the air entering each nozzle by inserting a standard pitot tube into a 2.5 cm or less diameter hole (see Figure 14-2) located in the manifold between each blast gate (or valve) and nozzle. Note that a standard pitot tube is used, rather than a type S, to eliminate possible velocity measurement errors due to cross-section blockage in the small (0.13 m diameter) manifold leg ducts. The pitot tube tip shall be positioned at the center

of each manifold leg duct. Take care to insure that there is no leakage around the pitot tube, which could affect the indicated velocity in the manifold leg. If the velocity of air being drawn into each nozzle is not the same, open or close each blast gate (or valve) until the velocity in each nozzle is the same. Fasten each blast gate (or valve) so that it will remain in this position and close the pitot port holes. This calibration shall be performed when the manifold system is installed. Alternatively, the manifold may be preassembled and the flow rates balanced on the ground, before being installed.

4.2 Periodical Performance Checks. Twelve months after their initial installation, check the calibration of the propeller anemometers, thermocouple-potentiometer system, and the recorders and/or counters as in Section 4.1. If the above systems pass the performance checks, (i.e., if no repair or replacement of any component is necessary), continue with the performance checks on a 12-month interval basis. However, if any of the above systems fail the performance checks, repair or replace the system(s) that failed and conduct the periodical performance checks on a 3-month interval basis, until sufficient information (consult with the Administrator) is obtained to establish a modified performance check schedule and calculation procedure.

Note: If any of the above systems fail the initial performance checks, the data for the past year need not be recalculated.

## 5. Procedure

### 5.1 Roof Monitor Velocity Determination.

5.1.1 Velocity Estimate(s) for Setting Isokinetic Flow. To assist in setting isokinetic flow in the manifold sample nozzles, the anticipated average velocity in the section of the roof monitor containing the sampling manifold shall be estimated prior to each test run. The tester may use any convenient means to make this estimate (e.g., the velocity indicated by the anemometer in the section of the roof monitor containing the sampling manifold may be continuously monitored during the 24-hour period prior to the test run).

If there is question as to whether a single estimate of average velocity is adequate for an entire test run (e.g., if velocities are anticipated to be significantly different during different potroom operations), the tester may opt to divide the test run into two or more "sub-runs," and to use a different estimated average velocity for each sub-run (see Section 5.3.2.2.)

5.1.2 Velocity Determination During a Test Run. During the actual test run, record the velocity or volumetric flowrate readings of each propeller anemometer in the roof monitor. Readings shall be taken for each anemometer every 15 minutes or at shorter equal time intervals (or continuously).

5.2 Temperature Recording. Record the temperature of the roof monitor every 2 hours during the test run.

### 5.3 Sampling.

5.3.1 Preliminary Air Flow in Duct. During 24 hours preceding the test, turn on the exhaust fan and draw roof monitor air through the manifold duct to condition the ductwork. Adjust the fan to draw a volumetric flow through the duct such that the velocity of gas entering the manifold nozzles approximates the average velocity of the air exiting the roof monitor in the vicinity of the sampling manifold.

### 5.3.2 Manifold Isokinetic Sample Rate Adjustment(s).

5.3.2.1 Initial Adjustment. Prior to the test run (or first sub-run, if applicable; see Sections 5.1.1 and 5.3.2.2), adjust the fan to provide the necessary volumetric flowrate in the sampling duct, so that air enters the manifold sample nozzles at a velocity equal to the appropriate estimated average velocity determined under Section 5.1.1. Equation 14-1 gives the correct stream velocity needed in the duct at the sampling location, in order for sample

gas to be drawn isokinetically into the manifold nozzles. Next, verify that the correct stream velocity has been achieved, by performing a pitot tube traverse of the sample duct (using either a standard or type S pitot tube); use the procedure outlined in Method 2.

$$V[d] = 8(D[n])^2 / (D[d])^2 (V[m]) 1 \text{ min} / 60 \text{ sec}$$

Eq. 14-1

Where:

$V[d]$  = Desired velocity in duct at sampling location, m/sec.

$D[n]$  = Diameter of a roof monitor manifold nozzle, m.

$D[d]$  = Diameter of duct at sampling location, m.

$V[m]$  = Average velocity of the air stream in the roof monitor, m/min, as determined under Section 5.1.1.

5.3.2.2 Adjustments During Run. If the test run is divided into two or more "sub-runs" (see Section 5.1.1), additional isokinetic rate adjustment(s) may become necessary during the run. Any such adjustment shall be made just before the start of a sub-run, using the procedure outlined in Section 5.3.2.1 above.

Note: Isokinetic rate adjustments are not permissible during a sub-run.

5.3.3 Sample Train Operation. Sample the duct using the standard fluoride train and methods described in Methods 13A and 13B. Determine the number and location of the sampling points in accordance with Method 1. A single train shall be used for the entire sampling run. Alternatively, if two or more sub-runs are performed, a separate train may be used for each sub-run; note, however, that if this option is chosen, the area of the sampling nozzle shall be the same (+/- 2 percent) for each train. If the test run is divided into sub-runs, a complete traverse of the duct shall be performed during each sub-run.

5.3.4 Time Per Run. Each test run shall last 8 hours or more; if more than one run is to be performed, all runs shall be of approximately the same (+/- 10 percent) length. If question exists as to the representativeness of an 8-hour test, a longer period should be selected. Conduct each run during a period when all normal operations are performed underneath the sampling manifold. For most recently-constructed plants, 24 hours are required for all potroom operations and events to occur in the area beneath the sampling manifold. During the test period, all pots in the potroom group shall be operated such that emissions are representative of normal operating conditions in the potroom group.

5.3.5 Sample Recovery. Use the sample recovery procedure described in Method 13A or 13B.

5.4 Analysis. Use the analysis procedures described in Method 13A or 13B.

## 6. Calculations

### 6.1 Isokinetic Sampling Check.

6.1.1 Calculate the mean velocity ( $V[m]$ ) for the sampling run, as measured by the anemometer in the section of the roof monitor containing the sampling manifold. If two or more sub-runs have been performed, the tester may opt to calculate the mean velocity for each sub-run.

6.1.2 Using Equation 14-1, calculate the expected average velocity ( $V[d]$ ) in the sampling duct, corresponding

to each value of V[m] obtained under Section 6.1.1.

6.1.3 Calculate the actual average velocity (V[s]) in the sampling duct for each run or sub-run, according to Equation 2-9 of Method 2, and using data obtained from Method 13.

6.1.4 Express each value V[s] from Section 6.1.3 as a percentage of the corresponding V[d] value from Section 6.1.2.

6.1.4.1 If V[s] is less than or equal to 120 percent of V[d], the results are acceptable (note that in cases where the above calculations have been performed for each sub-run, the results are acceptable if the average percentage for all sub-runs is less than or equal to 120 percent).

6.1.4.2 If V[s] is more than 120 percent of V[d], multiply the reported emission rate by the following factor.

$$1 + (100 V[s] / V[d] - 120) / 200$$

6.2 Average Velocity of Roof Monitor Gases. Calculate the average roof monitor velocity using all the velocity or volumetric flow readings from Section 5.1.2.

6.3 Roof Monitor Temperature. Calculate the mean value of the temperatures recorded in Section 5.2.

6.4 Concentration of Fluorides in Roof Monitor Air.

6.4.1 If a single sampling train was used throughout the run, calculate the average fluoride concentration for the roof monitor using Equation 13A-2 of Method 13A.

6.4.2 If two or more sampling trains were used (i.e., one per sub-run), calculate the average fluoride concentration for the run, as follows:

$$C[s] = \langle n \rangle \text{SIGMA } [i = 1] (F[t])[i] / \langle n \rangle \text{SIGMA } [i = 1] (V[m(\text{std})])[i]$$

Eq. 14-2

Where:

C[s] - Average fluoride concentration in roof monitor air, mg F/dscm (mg F/dscf).

F[t] = Total fluoride mass collected during a particular sub-run, mg F (from Equation 13A-1 of Method 13A or Equation 13B-1 of Method 13B).

V[m(std)] = Total volume of sample gas passing through the dry gas meter during a particular sub-run, dscm (dscf) (see Equation 5-1 of Method 5).

n = Total number of sub-runs.

6.5 Average volumetric flow from the roof monitor of the potroom(s) (or potroom segment(s)) containing the anemometers is given in Equation 14-3.

$$Q[sd] = V[mt]M[d]P[m](293 \text{ deg. K})A / (t[m] + 273 \text{ deg.})(760 \text{ mm Hg})$$

Eq. 14-3

Where:

$Q[\text{sd}]$  = Average volumetric flow from roof monitor at standard conditions on a dry basis,  $\text{m}^3/\text{min}$ .

$A$  = Roof monitor open area,  $\text{m}^2$ .

$V[\text{mt}]$  = Average velocity of air in the roof monitor,  $\text{m}/\text{min}$ , from Section 6.2.

$P[\text{m}]$  = Pressure in the roof monitor; equal to barometric pressure for this application,  $\text{mm Hg}$ .

$t[\text{m}]$  = Roof monitor temperature,  $\text{deg. C}$ , from Section 6.3.

$M[\text{d}]$  = Mole fraction of dry gas, which is given by:

$$M[\text{d}] = (1 - B[\text{ws}])$$

Note:  $B[\text{ws}]$  is the proportion by volume of water vapor in the gas stream, from Equation 5-3, Method 5.

## 6.6 Conversion Factors.

$$1 \text{ ft}^3 = 0.02832 \text{ m}^3$$

$$1 \text{ hr} = 60 \text{ min}$$

## 7. Bibliography

1. Shigehara, R. T., A Guideline for Evaluating Compliance Test Results (Isokinetic Sampling Rate Criterion). U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. August 1977.

## METHOD 15 -- DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES

### *Introduction*

The method described below uses the principle of gas chromatographic separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample-line loss criteria are met.

### *1. Principle and Applicability*

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide ( $\text{H}_2\text{S}$ ), carbonyl sulfide (COS), and carbon disulfide ( $\text{CS}_2$ ) by gas chromatographic (GC) separation and flame photometric detection (FPD).

1.2 Applicability. This method is applicable for determination of the above sulfur compounds from tail gas control units of sulfur recovery plants.

### *2. Range and Sensitivity*

2.1 Range. Coupled with a gas chromatographic system utilizing a 1-milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppm. It may be necessary to dilute gas samples from sulfur recovery plants hundred-fold (99:1) resulting in an upper limit of about 1000 ppm for each compound.

2.2 Sensitivity. The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppm for a 1 ml sample.

### 3. *Interferences*

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the probe, filter box, and connections, and by maintaining the SO<sub>2</sub> scrubber in an ice water bath. Moisture is removed in the SO<sub>2</sub> scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0 deg. C. Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO<sub>2</sub> have substantial desensitizing effects on the flame photometric detector even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting CO and CO<sub>2</sub> before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO<sub>2</sub> in the diluent gas. The CO<sub>2</sub> level should be approximately 10 percent for the case with CO<sub>2</sub> present. The two chromatograms should show agreement within the precision limits of Section 4.1.

3.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling system can lead to blockage of the particulate filter. This problem can be minimized by observing the filter for buildup and changing as needed.

3.4 Sulfur Dioxide (SO<sub>2</sub>). Sulfur dioxide is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO<sub>2</sub> scrubber described in Section 5.1.3 will effectively remove SO<sub>2</sub> from the sample.

3.5 Alkali Mist. Alkali mist in the emissions of some control devices may cause a rapid increase in the SO<sub>2</sub> scrubber pH to give low sample recoveries. Replacing the SO<sub>2</sub> scrubber contents after each run will minimize the chances of interference in these cases.

### 4. *Precision*

4.1 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than +/- 13 percent from the mean of the three injections.

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any run or series of runs within a 24-hour period shall not exceed +/- 5 percent.

### 5. *Apparatus*

#### 5.1 Sampling (Figure 15-1).

5.1.1 Probe. The probe shall be made of Teflon or Teflon-lined stainless steel and heated to prevent moisture condensation. It shall be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. The probe described in Section 2.1.1 of Method 16A having a nozzle directed away from the gas stream is recommended

for sources having particulate or mist emissions. Where very high stack temperatures prohibit the use of Teflon probe components, glass or quartz-lined probes may serve as substitutes.

NOTE. -- Mention of trade names or specific products does not constitute an endorsement by the Environmental Protection Agency.

5.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 deg. C (248 deg. F).

5.1.3 SO<sub>2</sub> Scrubber.

5.1.3.1 Three 300-ml Teflon segment impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3-mm (1/8-in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 deg. C. The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH.

5.1.3.2 Connections between the probe, particulate filter, and SO<sub>2</sub> scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO<sub>2</sub> scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120 C deg. (248 deg. F).

5.1.4 Sample Line. Teflon, no greater than 1.3-cm (1/2-in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

5.1.5 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless-steel. It must be capable of approximately a 9:1 dilution of the sample.

Figure 15-1. Sampling and dilution apparatus.

[SEE FIGURE IN ORIGINAL]

5.3 Gas Chromatograph (Figure 15-2). The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature +/- 1 deg. C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature +/- 1 deg. C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of  $10^{-9}$  to  $10^{-4}$  amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

Figure 15-2. Gas chromatographic flame photometric analyzer.

[SEE FIGURE IN ORIGINAL]

5.3.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas. The gas chromatograph shall be calibrated with the sample loop used for sample analysis.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H<sub>2</sub>S, COS, and CS<sub>2</sub>.

To demonstrate that adequate resolution has been achieved the tester must submit a chromatogram of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero +/- 5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5 Calibration System (Figure 15-3). The calibration system must contain the following components.

5.5.1 Flow System. To measure air flow over permeation tubes within +/- 2 percent. Each flowmeter shall be calibrated after a complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by more than 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that will yield the lowest flow measurement. Calibration with a wet-test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

5.5.2 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 deg. C.

5.5.3 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 0.1 deg. C.

Figure 15-3. Apparatus for field calibration.

[SEE FIGURE IN ORIGINAL]

## 6. Reagents

6.1 Fuel. Hydrogen (H<sub>2</sub>) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O<sub>2</sub>) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H<sub>2</sub>S, COS, and CS<sub>2</sub>, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall

at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

6.6 Citrate Buffer. Dissolve 300 g of potassium citrate and 41 g of anhydrous citric acid in 1 liter of water. Alternatively, 284 g of sodium citrate may be substituted for the potassium citrate. Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

6.7 Sample Line Loss Gas (Optional). As an alternative, H<sub>2</sub>S cylinder gas may be used for the sample line loss test. The gas shall be calibrated against permeation devices having known permeation rates or by the procedure in Section 7 of Method 16A.

## 7. *Pretest Procedures*

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak. As an alternative to the initial leak-test, the sample line loss test described in Section 10.1 may be performed to verify the integrity of components.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

## 8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within +/- 0.1 deg. C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of Section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K \times P[r] / ML$$

Eq. 15-1

Where:

C = Concentration of permeant produced in ppm.

P[r] = Permeation rate of the tube in  $\mu$ g/min.

M = Molecular weight of the permeant: g/g-mole.

L = Flow rate, l/min, of air over permeant at 20 deg. C, 760 mm Hg.

K = Gas constant at 20 deg. C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of Analysis System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppm for a 1-ml sample) for each of the three major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in Section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data. Alternatively, a least squares equation may be generated from the calibration data using concentrations versus the appropriate instrument response units.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in Section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for

H<sub>2</sub>S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this section. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of Section 4.1 are still applicable.

## 9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in section 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe or Filter. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter. If either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning or replacing the probe and filter. After each run, the probe and filter shall be inspected and, if necessary, replaced.

## 10. Post-Test Procedures

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, +/- 20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling losses of 0-20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in nitrogen and verified according to Section 6.7 may be used. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H<sub>2</sub>S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under Section 10.2. The calibration drift should not exceed the limits set forth in Section 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

## 11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of SO<sub>2</sub> Equivalent. SO<sub>2</sub> equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis.

SO<sub>2</sub> equivalent = SIGMA (H<sub>2</sub>S, COS, 2 CS<sub>2</sub>)d

Eq. 15-2

Where:

SO<sub>2</sub> equivalent = The sum of the concentration of each of the measured compounds (COS, H<sub>2</sub>S, CS<sub>2</sub>) expressed as sulfur dioxide in ppm.

H<sub>2</sub>S = Hydrogen sulfide, ppm.

COS = Carbonyl sulfide, ppm.

CS<sub>2</sub> = Carbon disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average SO<sub>2</sub> Equivalent. This is determined using the following equation. Systems that do not remove moisture from the sample but conditions the gas to prevent condensation must correct the average SO<sub>2</sub> equivalent for the fraction of water vapor present.

Average SO<sub>2</sub> equivalent =  $\frac{\sum_{i=1}^N \text{SO}_2 \text{ equiv}[i]}{N}$

Eq. 15-3

where:

Average SO<sub>2</sub> equivalent = Average SO<sub>2</sub> equivalent in ppm, dry basis.

Average SO<sub>2</sub> equivalent [i] = SO<sub>2</sub> in ppm as determined by Equation 15-2.

N = Number of analyses performed.

## 12. Bibliography

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APPENDIX A CONTINUED