State of California
AIR RESOURCES BOARD

Resolution 83-14

June 29, 1983

Agenda Item No.: 83-8-1

WHEREAS, Section 39601 of the Health and Safety Code authorizes the Air Resources Board ("Board") to adopt standards, rules, and regulations necessary for the proper execution of the powers and duties granted to and imposed upon the Board by law;

WHEREAS, Section 39607(d) of the Health and Safety Code requires the Board to adopt test procedures to measure compliance with its nonvehicular emission standards and those of the air pollution control and management districts;

WHEREAS, the Board's staff has developed sixteen test methods for determining compliance with district nonvehicular (stationary source) emission standards;

WHEREAS, the test methods have been thoroughly field tested by the Board's staff;

WHEREAS, the California Environmental Quality Act and Board regulations require that no project having significant adverse environmental impacts be adopted as proposed if feasible alternatives or mitigation measures are available which would substantially reduce such adverse impacts;

WHEREAS, a public hearing and other administrative proceedings have been held in accordance with the provisions of the Administrative Procedure Act (Government Code, Title 2, Division 3, Part 1, Chapter 3.5); and

WHEREAS, the Board finds that:

> Adoption of the sixteen test methods set forth in Attachment A, and adoption of regulations incorporating the test methods, set forth in Attachment B, is necessary and appropriate to satisfy the requirements of Section 39607(d) of the Health and Safety Code and may simplify the identification, adoption and enforcement of nonvehicular emission standards;
>
> Adoption of Section 94100, Title 17, California Administrative Code, set forth in Attachment B, is necessary to assure that a specified test method is applicable to all situations covered by one of the sixteen test methods, while providing the districts the flexibility of using their own methods if they wish; and
>
> The adoption of the test methods and regulations set forth in Attachments A and B will have no significant adverse environmental impacts.

NOW, THEREFORE, BE IT RESOLVED that the Board hereby adopts the sixteen test methods for determining compliance with district nonvehicular (stationary source) emission standards set forth in Attachment A.

BE IT FURTHER RESOLVED that the Board hereby adopts Sections 94100 through 94116, Title 17, California Administrative Code, as set forth in Attachment B hereto.

I certify that the above is a true and correct copy of Resolution 83-14 as adopted by the Air Resources Board.

Harold Holmes

Harold Holmes, Board Secretary

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^2 (113 $in.^2$) in 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 Control Agency's authorized representative.

2. Procedure

2.1 Selection of Measurement Site. Sampling or velocity measurement is performed at a site located at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack, or from a visible flame. If necessary, an alternative location may be selected, at a position at least two stack or duct diameters downstream and a half diameter upstream from any flow disturbance. For a rectangular cross section, an equivalent diameter (D_e) shall be calculated from the following equation, to determine the upstream and downstream distances: $D_e = \frac{2LW}{L + W}$ where L = length and W = width.

2.2 Determining the Number of Traverse Points

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

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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.

Subject to the approval of the Control Agency's authorized representative, the minimum number of traverse points may be less than that determined from Figure 1-1 to accommodate specific test situations.

TABLE 1-1. Cross-sectional 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

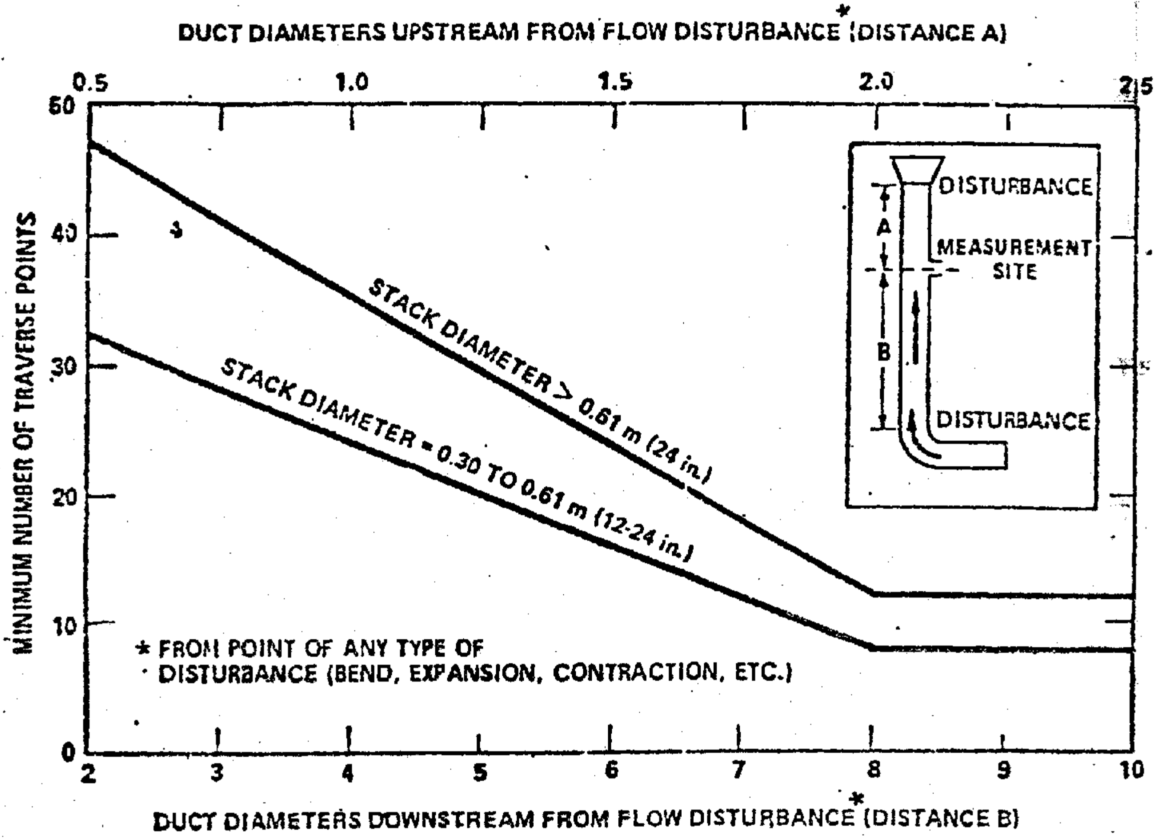


Figure 1-1. Minimum number of traverse points for particulate traverses.

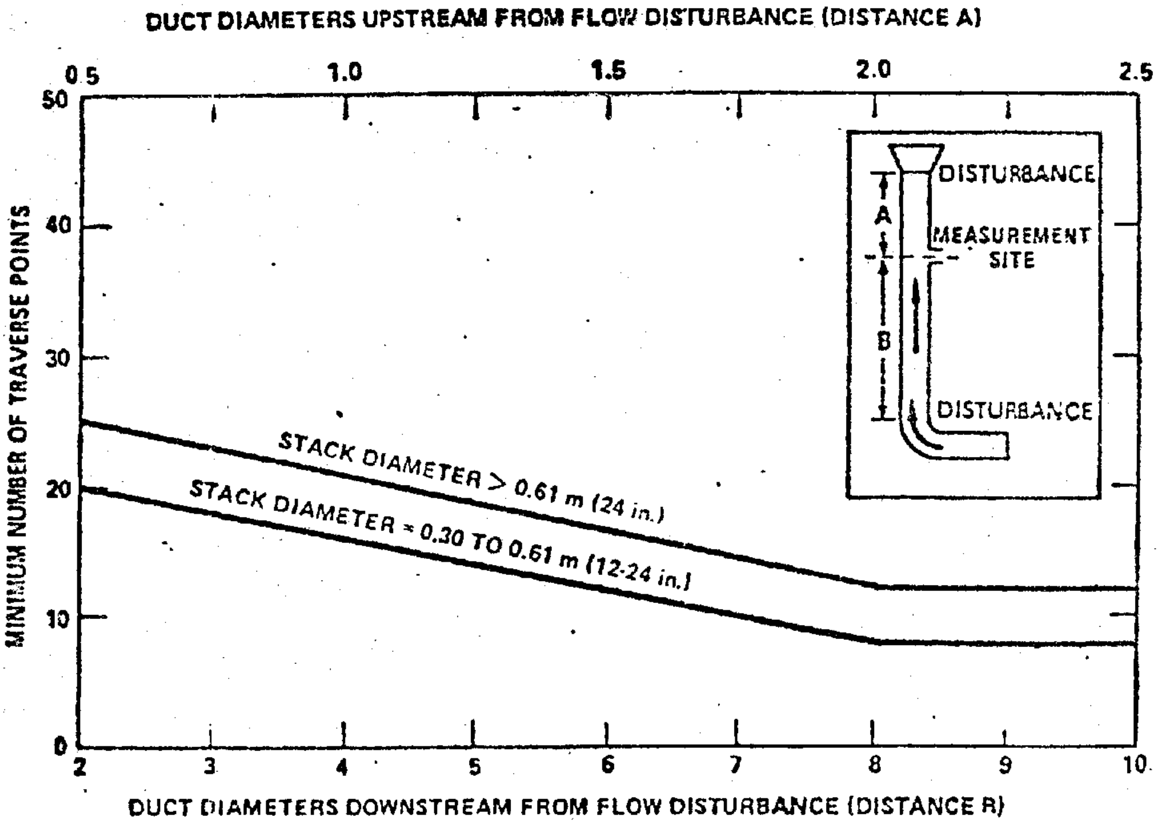
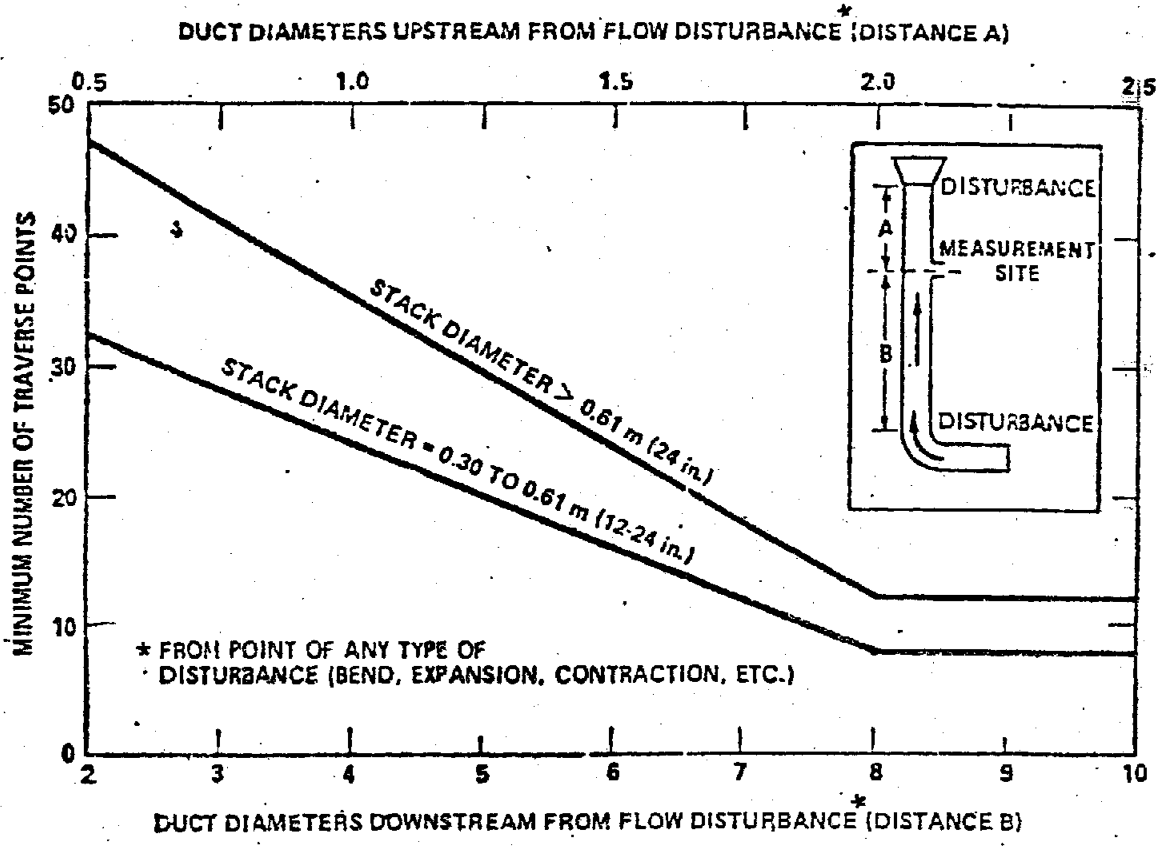


Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.



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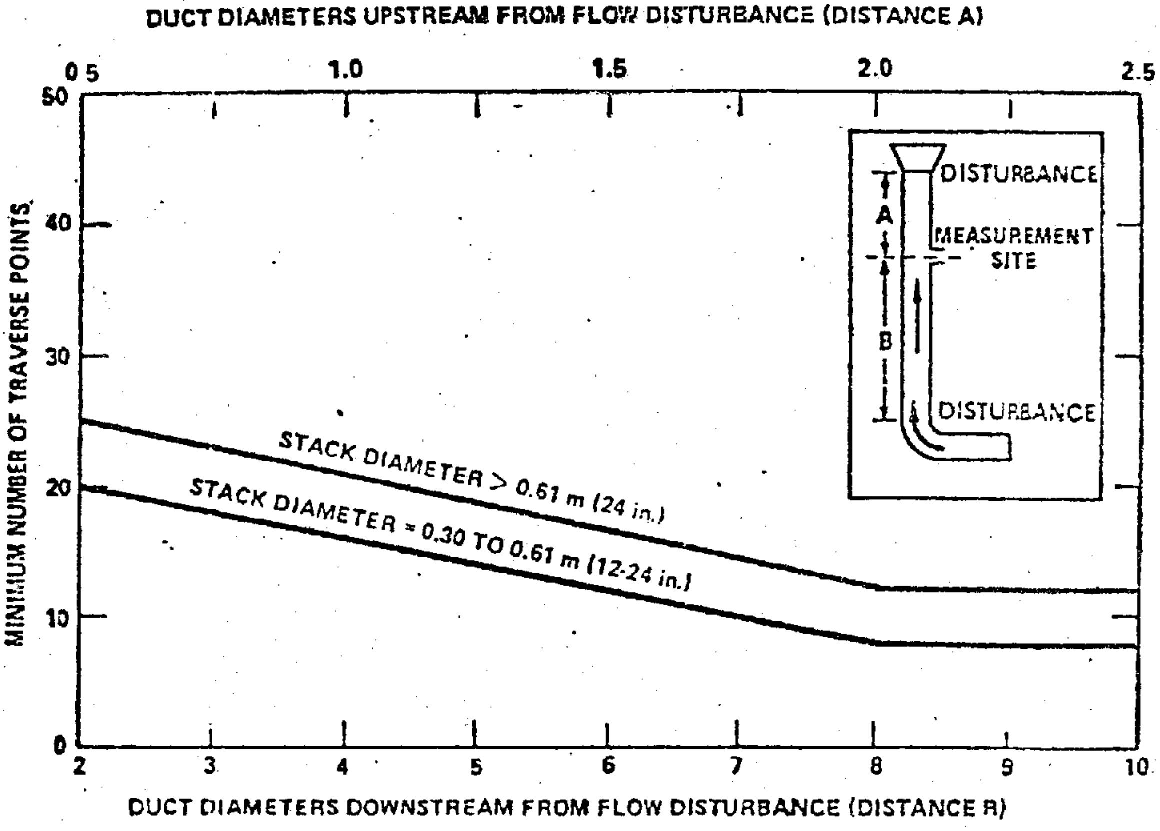

Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

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

Subject to the approval of the Control Agency's authorized representative, the minimum number of traverse points may be less than that determined from Figure 1-2 to accommodate specific test situations.

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 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 Control Agency's authorized representative.

Table 1-2. Location of traverse points in circular stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.5	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	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

TRAVERSE POINT	DISTANCE, % of diameter
1	4.4
2	14.7
3	29.5
4	70.5
5	85.3
6	95.6

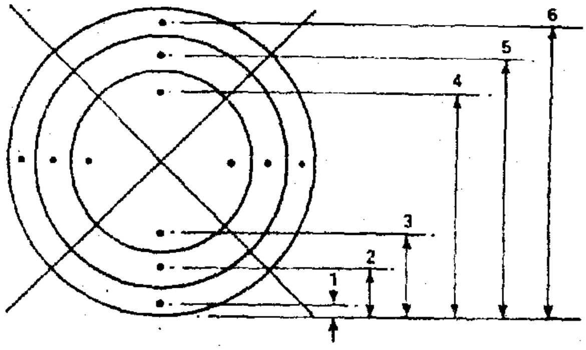

Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

Table 1-2. Location of traverse points in circular stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	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
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TRAVERSE POINT	DISTANCE, % of diameter
1	4.4
2	14.7
3	29.5
4	70.5
5	85.3
6	95.6

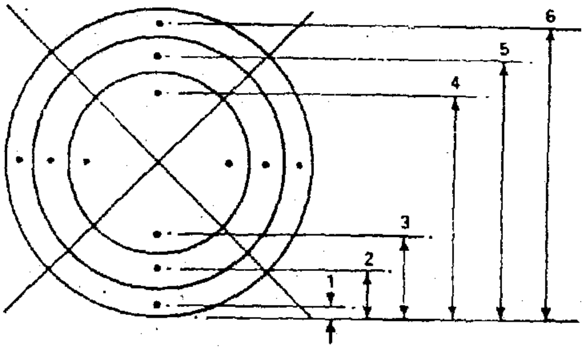

Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

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 transverse 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.

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, 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.

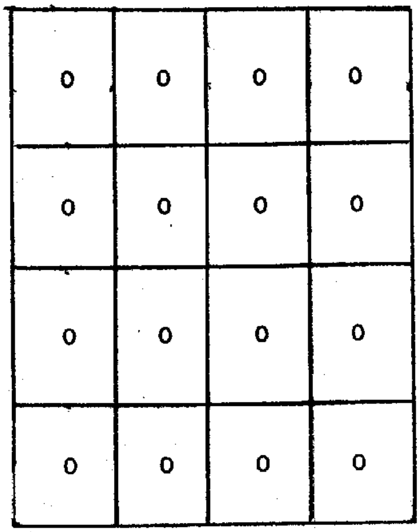

Figure 1-4
Example Showing Rectangular Stack Cross
Section Divided into Twelve Equal Areas, with a Traverse
Point at Centroid of Each Area

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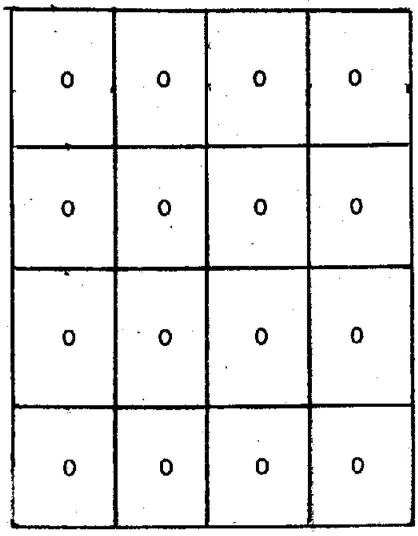

Figure 1-4
Example Showing Rectangular Stack Cross
Section Divided into Twelve Equal Areas, with a Traverse
Point at Centroid of Each Area

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.

Subject to the approval of the Control Agency's authorized representative, alternatives to the matrix layout prescribed in Table 1-1 may be used to accommodate specific test situations.

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 Control Agency's authorized representative 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.

Level and zero the manometer. Connect a Type S pitot tube to the manometer. Position the Type S pitot tube at each traverse point, in succession, so that the planes of the face openings of the pitot tube are perpendicular to the stack cross-sectional plane: when the Type S pitot tube is in this position it is at "0 reference." Note the differential pressure (% p) reading at each traverse point. If a null (zero) pitot reading is obtained at 0° reference at a given traverse point, an acceptable flow condition exists at that point. If the pitot reading is not zero at 0° reference, rotate the pitot tube (up to î 90° yaw angle), until a null reading is obtained. Carefully determine and record the value of the rotation angle (a) to the nearest degree. After the null technique has been applied at each traverse point, calculate the average of the absolute values of a; assign a value of 0° to those points for which no rotation was required, and include these in the overall average. If the average value of a is greater than 10° the overall flow condition in the stack is unacceptable and alternative methodology, subject to the approval of the Control Agency's authorized representative must be used to perform accurate sample and velocity traverses.

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3. Bibliography

1. Determining Dust Concentration in a Gas Stream. ASME. Performance Test Code No. 27. New York, 1957.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District. Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co. Los Angeles, CA. Bulletin WP-50. 1968.

4. Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Book of ASTM Standards, Part 23. ASTM Designation D-2928-71. Philadelphia, PA. 1971.

5. Hanson, H.A., et al. Particulate Sampling Strategies for Large Power Plants Including Nonuniform Flow. USEPA, ORD, ESRL, Research Triangle Park, NC. EPA-600/2-76-170. June 1976.

6. Entropy Environmentalists, Inc. Determination of the Optimum Number of Sampling Points: An Analysis of Method 1 Criteria. Environmental Protection Agency. Research Triangle Park, NC. EPA Contract No. 68-01-3172, Task 7.

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 Control Agency's Authorized Representative, 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 Control Agency's Authorized Representative) to be capable of meeting the specifications will be considered acceptable.

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

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

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

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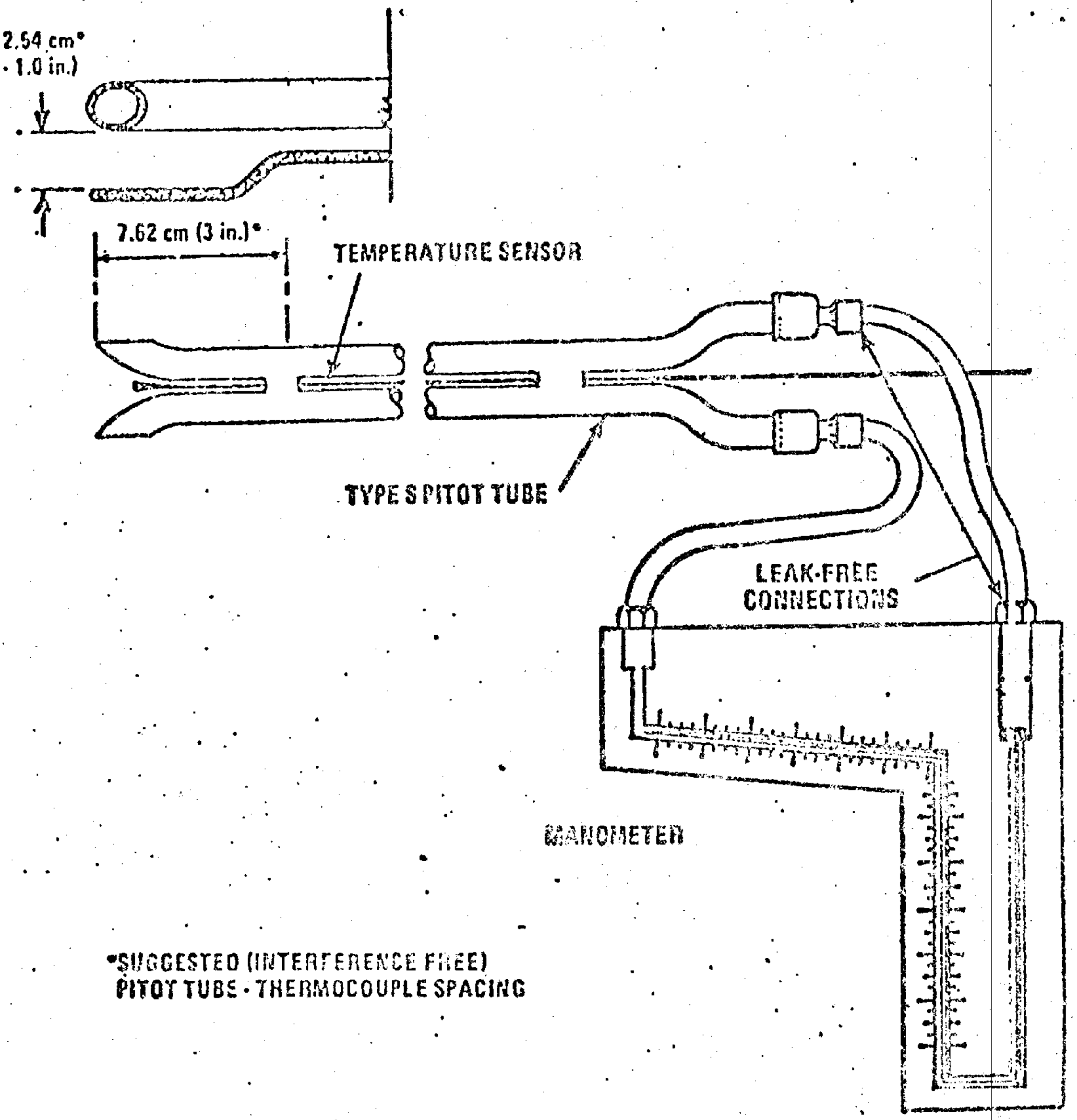

*SUGGESTED (INTERFERENCE FREE)
PITOT TUBE - THERMOCOUPLE SPACING

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

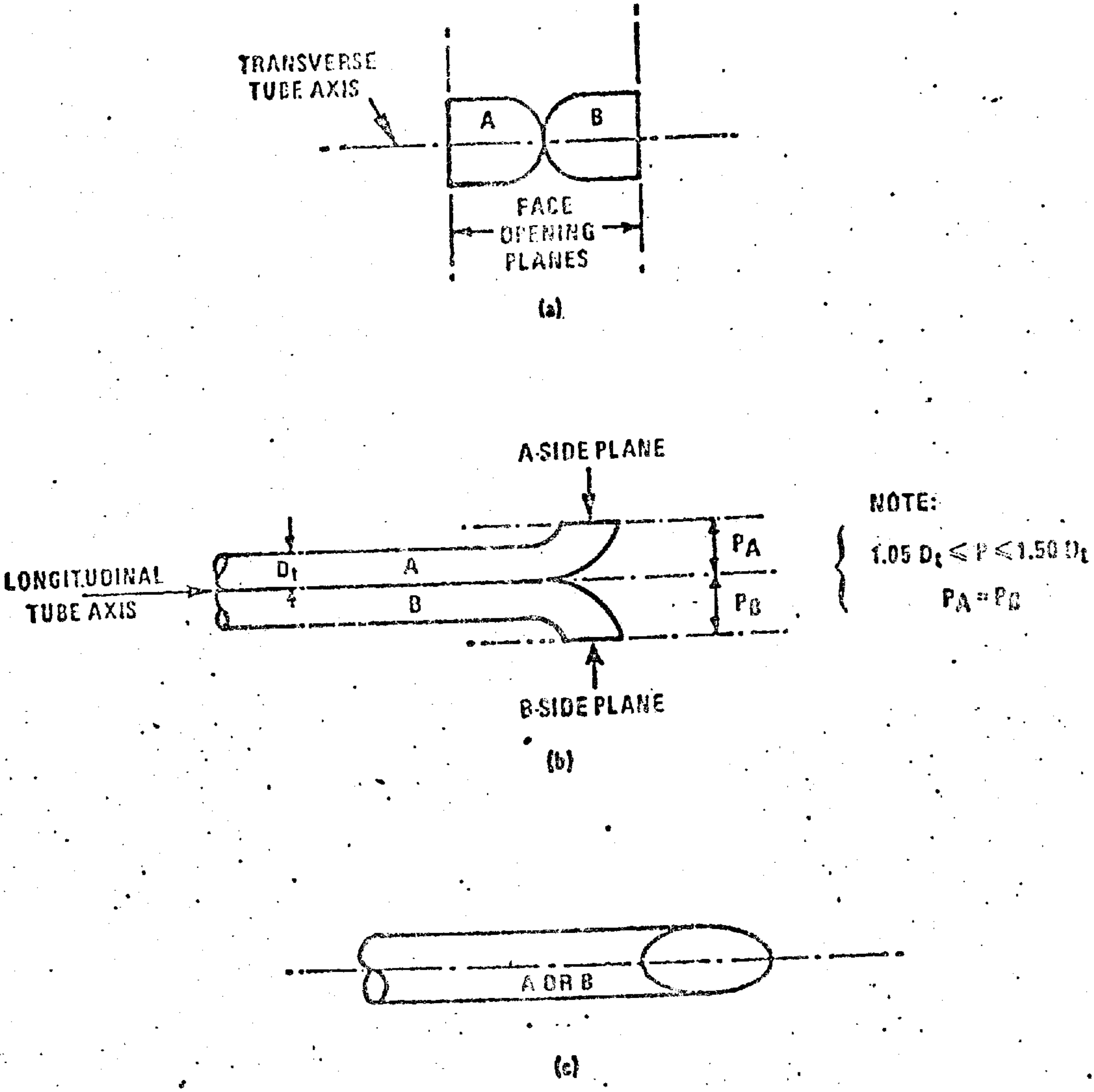

Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline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

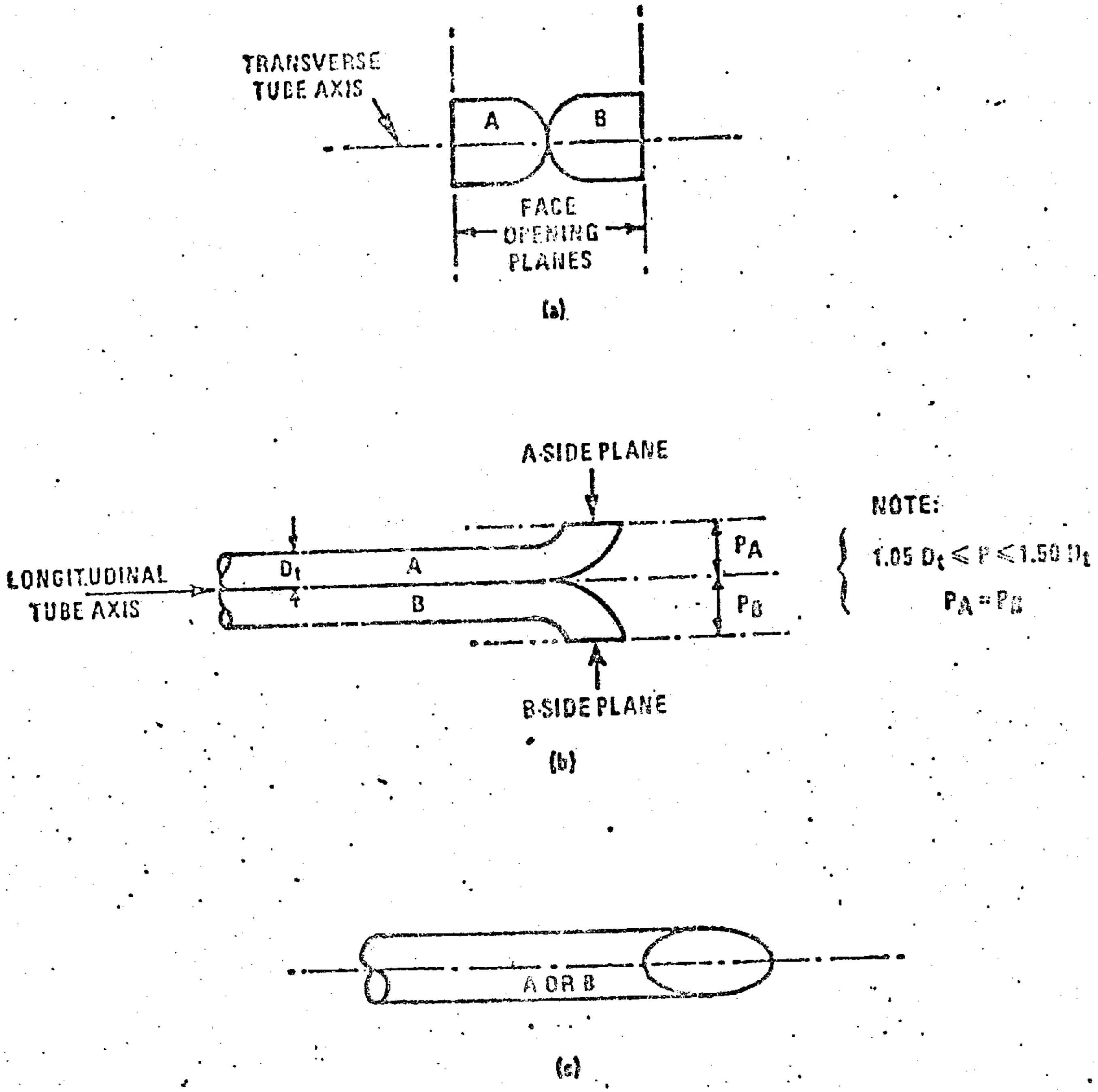

Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline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

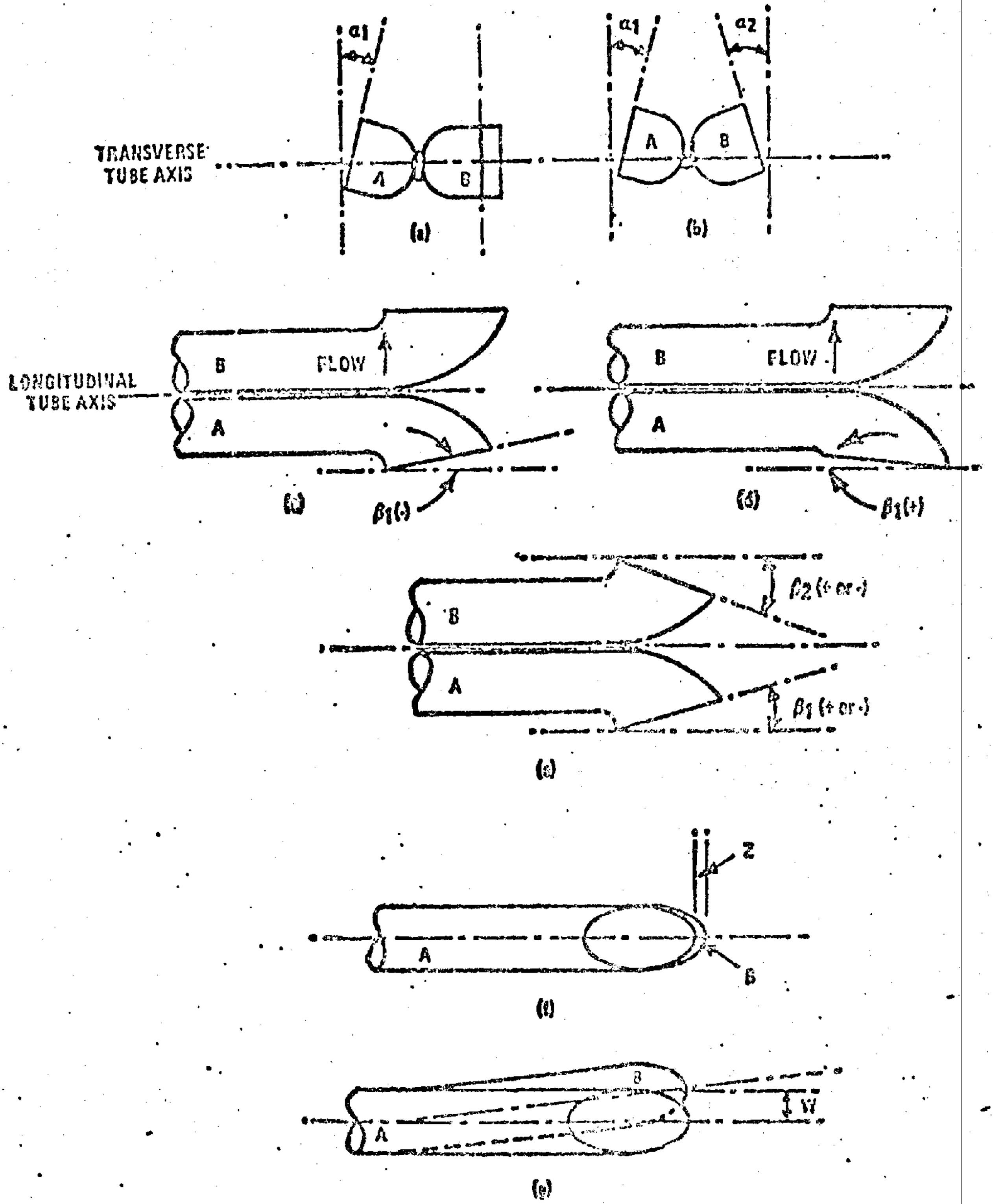

Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of $\bar{C}_{p(s)}$ so long as α_1 and $\alpha_2 < 10^\circ$, β_1 and $\beta_2 < 5^\circ$, $z < 0.32$ cm (1/8 in.) and $w < 0.08$ cm (1/32 in.) (citation 11 in Section 6).

streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (Δp) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another Δp reading. If the 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 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 Δp readings shall be taken, as above, for the last two back purges at which suitably high 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_2O divisions on the 0- to 1-in. inclined scale, and 0.1-in. H_2O divisions on the 1- to 10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H_2O. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Control Agency's Authorized Representative), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (Δp) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another Δp reading. If the 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 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 Δp readings shall be taken, as above, for the last two back purges at which suitably high p readings are observed.

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1.3 mm (0.05 in.) H_2O; (2) for traverses of 12 of more points, more than 10 percent of the individual Δp readings are below 1.3 mm (0.05 in.) H_2O; (3) for traverses of fewer than 12 points, more than one Δp reading is below 1.3 mm (0.05 in.) H_2O.

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

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

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

n = Total number of traverse points.

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

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

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

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

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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 Method 4 or Method 5 equipment for moisture content determination; other methods may be used subject to approval of the Control Agency's Authorized Representative.

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 criterion given in 2.7.1 through 2.7.5 below and illustrated in Figure 2.4 (see also Citations 7, 8, and 17 in Section 6) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 ±0.01.

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

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

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

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

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2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type S Pitot Tube Calibration

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

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 p fluctuations. Conduct a pretest leak-check as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3 in. H_2O) velocity pressure registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3 in. H_2O). Other leak-check procedures, subject to the approval of the Control Agency's Authorized Representative, may be used.

2.7.5 Ninety degree bend, with curved or mitered junction.

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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 or similar 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 p values encountered (see Section 2.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the 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.

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

VELOCITY TRAVERSE DATA

Traverse Point Number	Velocity Head in. H_2O	Distance from inside wall (in.)	Stack Temperature (T_s), °F	Velocity Head in. H_2O	$\sqrt{\Delta P}$	Stack Temperature (T_s), °F
Average						

Plant ______________________________

Pitot Tube Factor --------

Sampling Site ______________________________

Remarks ______________________________

____

Barometric Pressure, in. Hg ______________

Static Pressure in Stack (P_g) in. Hg __________

Operators ____________ Date ____________

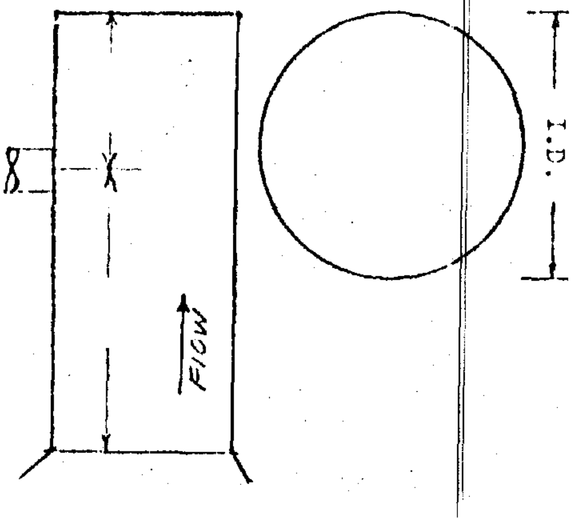

FIGURE 2-5 VELOCITY TRAVERSE DATA

VELOCITY TRAVERSE DATA

Traverse Point Number	Velocity Head in. H_2O	Distance from inside wall (in.)	Stack Temperature (T_s), °F	Velocity Head in. H_2O	$\sqrt{\Delta P}$	Stack Temperature (T_s), °F
Average						

Plant ____________________

Pitot Tube Factor ________

Sampling Site ____________________

Remarks ____________________

____

Barometric Pressure, in. Hg ____________________

Static Pressure in Stack (P_s) in. Hg ____________________

Operators ____________ Date ____________

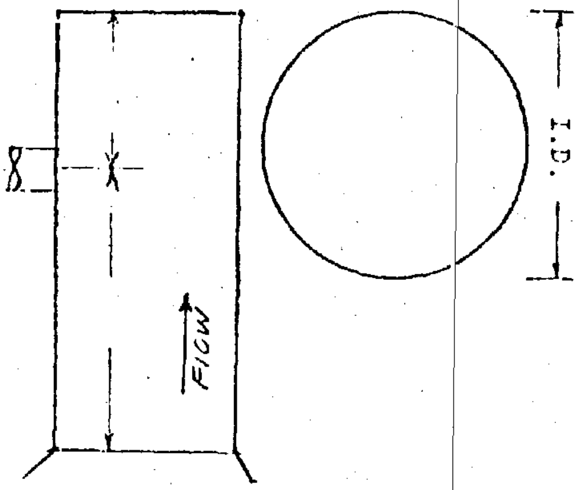

FIGURE 2-5 VELOCITY TRAVERSE DATA

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 $\underline{D}_t$, 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 Section 6); therefore, an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly.

The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2-6 through 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-6 through 2-8 shall be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, and prior to calibration, the

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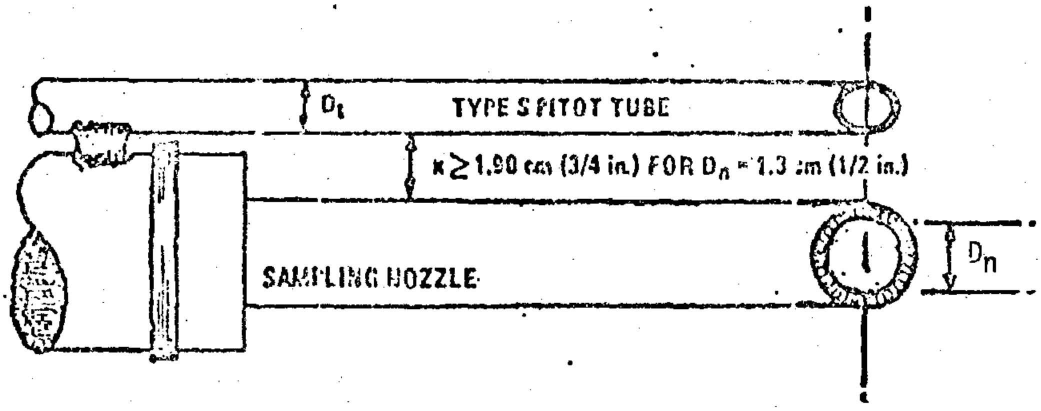
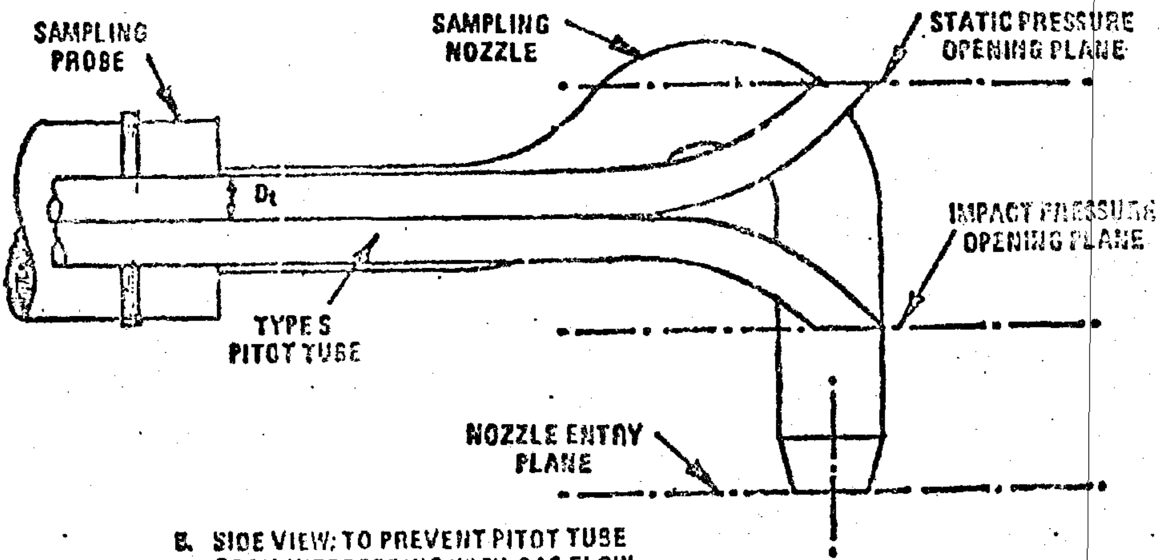


A. BOTTOM VIEW; SHOWING MINIMUM PITOT-NOZZLE SEPARATION.



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

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

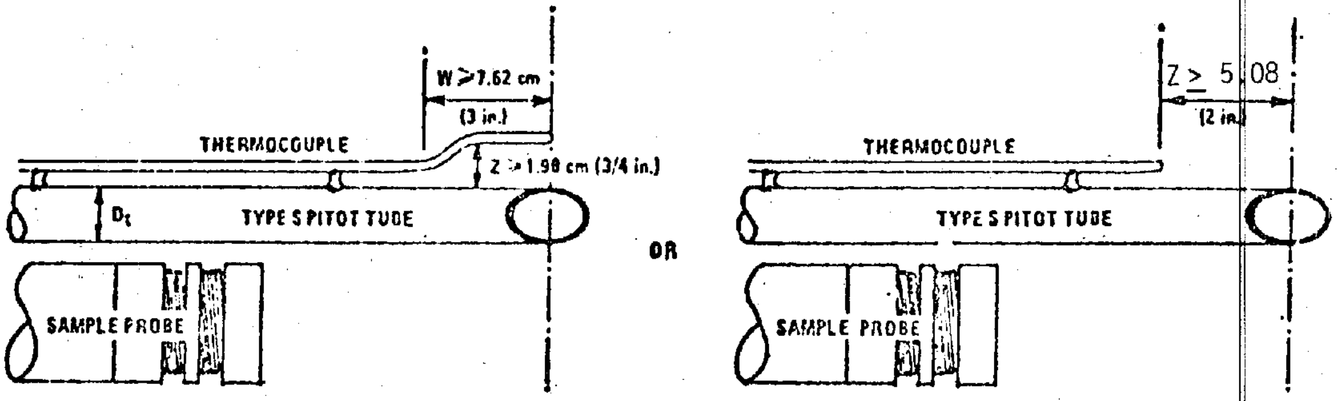


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

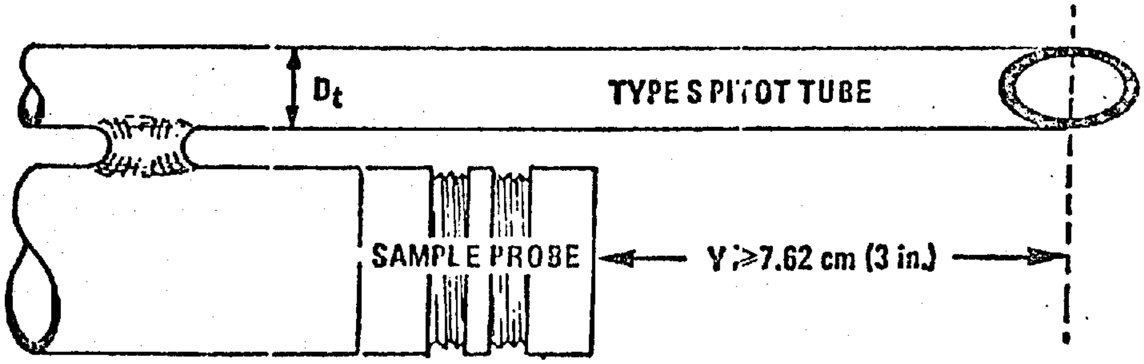
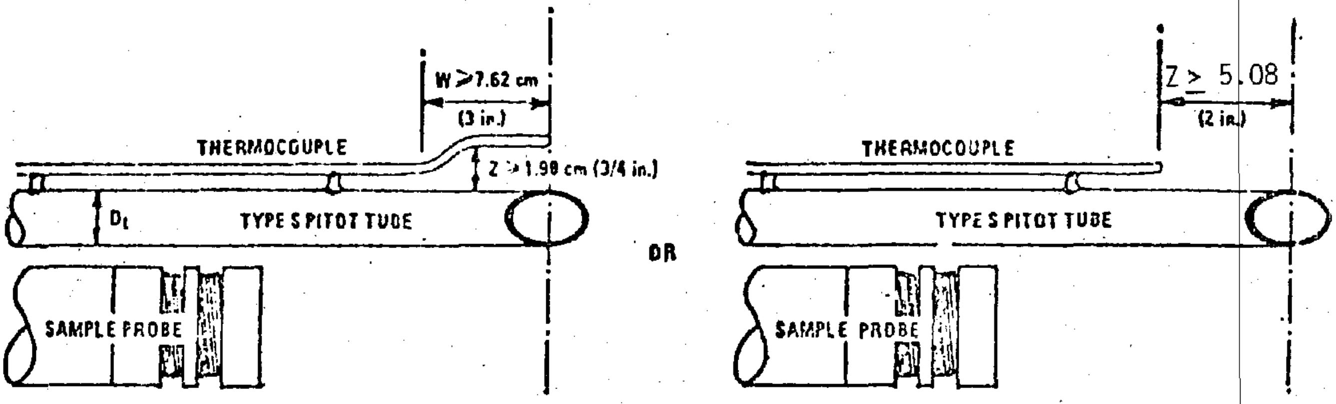


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).



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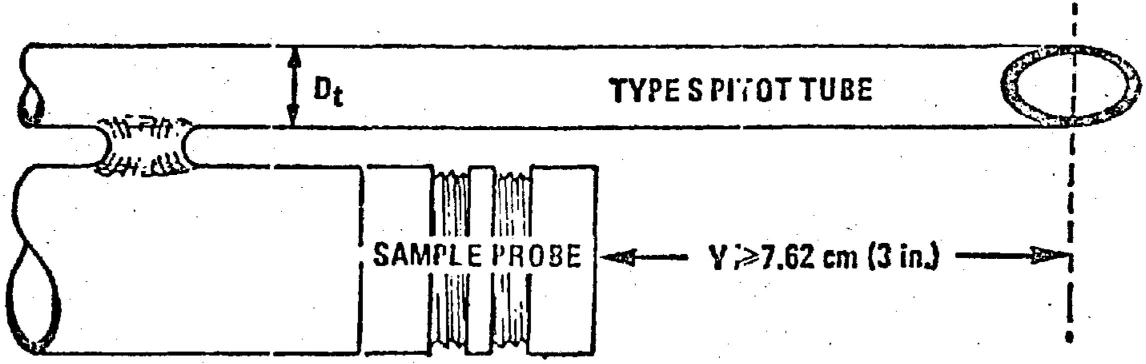

Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

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:

4.1.2.1 The flowing gas stream must be confined to a duct 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:

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

Equation 2-1

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

To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located 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 Control Agency's Authorized Representative), 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 following equation, to determine the number of duct diameters:

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Equation 2-1

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

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

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

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

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.

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

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

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

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

4.1.3.8 Repeat steps 4.1.3.2 through 4.1.3.7 above for the B side of the Type S pitot tube.

PITOT TUBE IDENTIFICATION NUMBER: ________________ DATE: ____________

CALIBRATED BY: ____

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

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

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

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

Figure 2-9. Pitot tube calibration data.

PITOT TUBE IDENTIFICATION NUMBER: ____________________ DATE: ____________

CALIBRATED BY: ____

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

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

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

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

Figure 2-9. Pitot tube calibration data.

4.1.3.9 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 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:

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

Equation 2-2

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

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

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

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

4.1.4.2 Calculate $\overline{C}_p$ (side A), the mean A side coefficient, and $\overline{C}_p$ (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 $\overline{C}_p$ (side A), and the deviation of each B-side value of $C_{p(s)}$ from $\overline{C}_p$ (side B). Use the following equation:

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

Equation 2-3

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

$$a(\text{side A or B}) = \frac{\sum_{1}^{3} [C_{p(\overline{s})} - C_p(\text{A or B})]}{3}$$

Equation 2-4

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

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

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$$a(\text{side A or B}) = \frac{\sum_{1}^{3} [C_{p(\overline{s})} - C_p(\text{A or B})]}{3}$$

Equation 2-4

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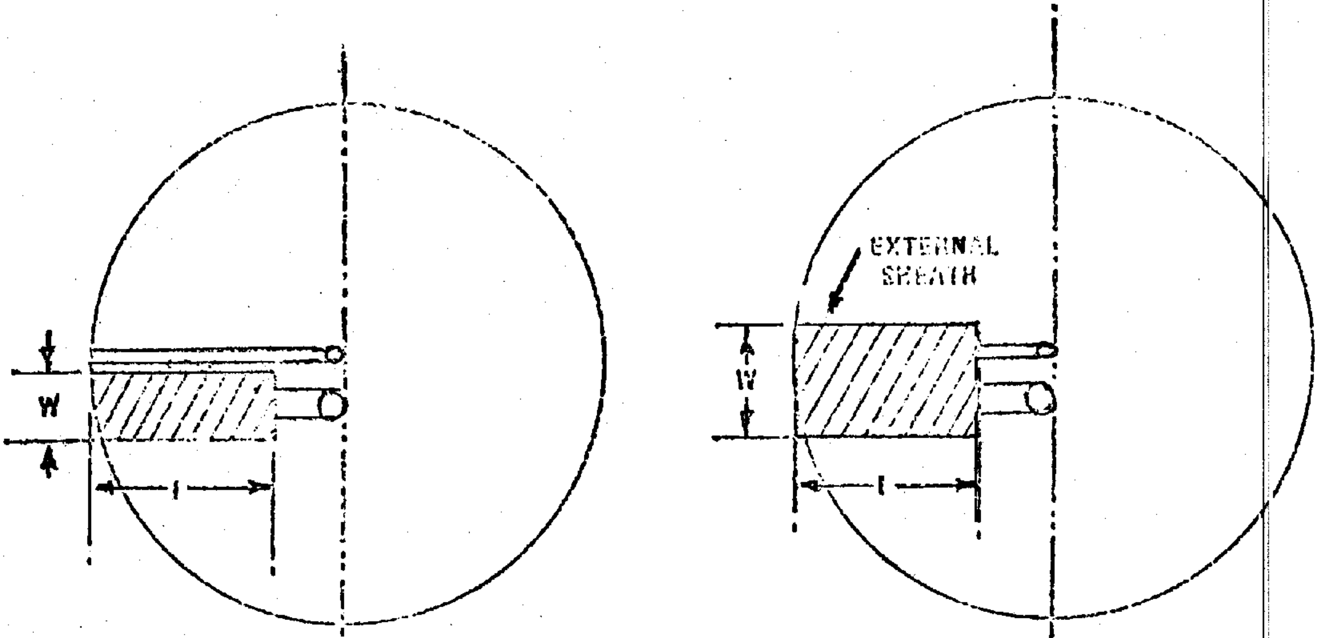
4.1.5.1.2 For Type S pitot tube-thermocouple combinations (without sample probe), select a calibration point at or near the center of the duct;, and follow the procedures outlined in Section 4.1.3 and 4.1.4 above. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination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

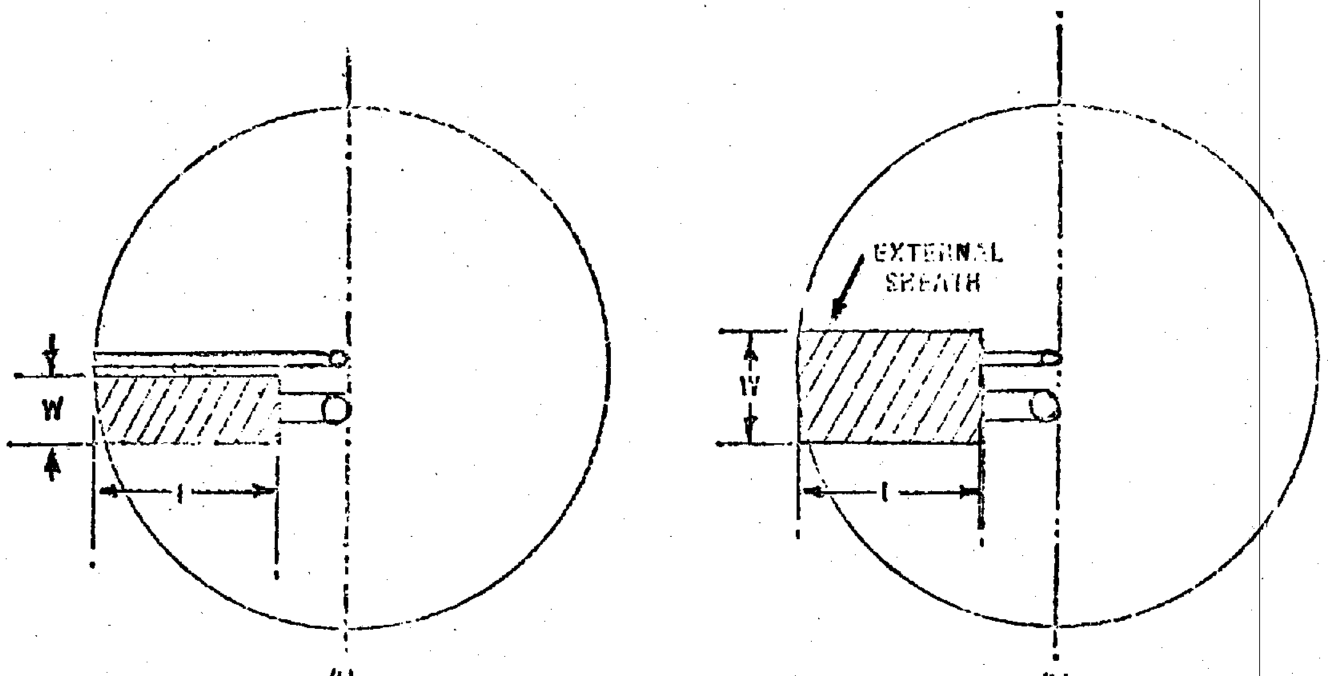
4.1.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of the probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values (Citation 9). Therefore, to minimize 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 two percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and three percent or less for assemblies with external sheaths (Figure 2-10b).



(b) (b)

$$\text{ESTIMATED SHEATH BLOCKAGE (\%)} = \left[\frac{l \times W}{\text{DUCT AREA}}\right] \times 100$$

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



(b)

(b)

$$\text{ESTIMATED SHEATH BLOCKAGE (\%)} = \left[\frac{l \times W}{\text{DUCT AREA}}\right] \times 100$$

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

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. (Citation 9 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 (a) value of 0.01 or less (see Section 4.1.4.4).

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 $C_{p(s)}$. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches. (Citation 16 in Section 6.)

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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 Control Agency's Authorized Representative).

4.3 Temperature Gauges. After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other gauges at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405°C (761°F), use an NBS-calibrated reference thermocouple-potentiometer system or an alternate reference, subject to the approval of the Control Agency's Authorized Representative.

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 necessary). If the intercomponent spacings have changed, restore the original spacings or recalibrate the assembly.

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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 Control Agency's Authorized Representative.

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^2 (ft^2).

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

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant.

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

for the metric system and

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

for the English system.

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

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

= M_d (1-Bws) + 18.0 Bws

Equation 2-5

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

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

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

= $P_{bar} + P_g$

Equation 2-6

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

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

t_s = Stack temperature ^{o}C (^{o}F).

T_s = Absolute stack temperature, ^{o}K (^{o}R).

= 273 + t_s for metric

Equation 2-7

= 460 + t_s for English

Equation 2-8

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

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

p = Velocity head of stack gas, mm H_2O (in. H_2O).

3,600 = Conversion factor, sec/hr.

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

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).

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

1. Principle and Applicability

1.1 Principle: A gas sample is extracted from a stack, by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO_2), percent oxygen (O_2), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite[1/] analyzer or other analyzers specified in Method 100 may be used for the analysis; for excess air or emission rate correction factor determination, an Orsat analyzer or analyzers specified in Method 100 must be used.

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

[1/] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

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

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 Control Agency's Authorized Representative.

2.1 Grab Sampling (Figure 3-1)

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a

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2.1 Grab Sampling (Figure 3-1)

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

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

2.2 Integrated Sampling (Figure 3.2)

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

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

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

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

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

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

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O) and allow to stand overnight. A deflated bag indicates a leak.

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

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

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

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

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

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O) and allow to stand overnight. A deflated bag indicates a leak.

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

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

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

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

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

3. Dry Molecular Weight Determination

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

3.1 Single-Point, Grab Sampling and Analytical Procedure

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

3.1.2 Set up the equipment as shown in Figure 3.1, making sure all connections ahead of the analyzer are tight and leak-free. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in Section 5.

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

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

Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure

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

3.2.2 Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag.

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

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

Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure

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

3.2.2 Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag.

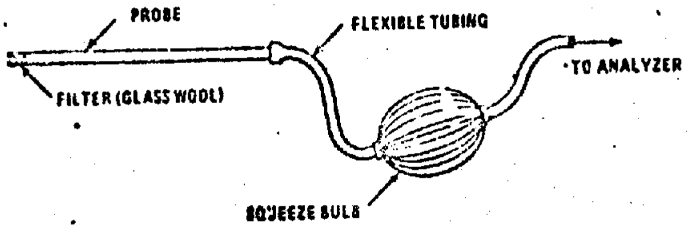

Figure 3-1. Grab-sampling train.

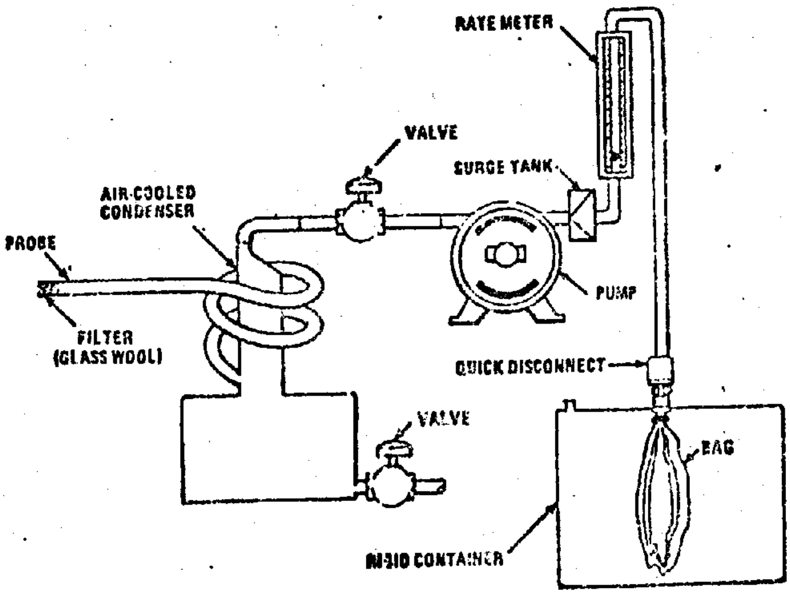

Figure 3-2. Integrated gas sampling train.

TIME	TRAVERSE PT.	Q lpm	% DEV.[a]
	AVERAGE		

[a] $\% \text{ DEV} = \left(\frac{Q - Q_{avg}}{Q_{avg}}\right) 100$ (MUST BE $<$10%)

Figure 3-3. Sampling rate data.

Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak-free.

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

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

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

Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak-free.

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

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

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

Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

3.3 Multi-Point, Integrated Sampling and Analytical Procedure

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

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

4. Emission Rate Correction Factor or Excess Air Determination

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

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

4.1 Single Point, Grab Sampling and Analytical Procedure

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

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

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

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 Control Agency's Authorized Representative.

4.1 Single Point, Grab Sampling and Analytical Procedure

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

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

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

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

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. Note: Since this single-point, grab sampling and analytical procedure 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_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure

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

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

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

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-checked (see Section 5) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after

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

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

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

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

4.2.6 Repeat the analysis until the following criteria are met:

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

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

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

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.
Note: Although in most instances only CO_2 or O_2; is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure

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

than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2 and report the results to the nearest 0.1 percent.

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

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.
Note: Although in most instances only CO_2 or O_2; is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure

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

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

5. Leak-Check Procedure for Orsat Analyzers

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:

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

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

5.1.3 Record the meniscus position.

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

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

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

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

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

6. Calculations

6.1 Nomenclature.

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

Percent EA = Percent excess air.

Percent CO_2 = Percent CO_2 by volume (dry basis).

Percent O_2 = Percent O_2 by volume (dry basis).

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

Percent N_2 = Percent N_2 by volume (dry basis).

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

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

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100

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

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

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

6. Calculations

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Percent CO_2 = Percent CO_2 by volume (dry basis).

Percent O_2 = Percent O_2 by volume (dry basis).

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

Percent N_2 = Percent N_2 by volume (dry basis).

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

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

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100

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

$$\text{percent EA} = \left[\frac{\text{percent } O_2 - 0.5 \text{ percent CO}}{0.264 \text{ percent } N_2 - \text{percent } O_2 + 0.5 \text{ percent CO}}\right] 100$$

Equation 3-1

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

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

$$M_d = 0.440 (\text{percent } CO_2) + 0.320 (\text{percent } O_2) + 0.280 (\text{percent } N_2 + \text{percent CO})$$

Equation 3-2

Note: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 37.7). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Control Agency's Authorized Representative.

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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 results of the approximation method, unless the approximation method is shown, to the satisfaction of the Control Agency's Authorized Representative, to be capable of yielding results within 1 percent H_2O 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°C (2°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 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 results of the approximation method, unless the approximation method is shown, to the satisfaction of the Control Agency's Authorized Representative, to be capable of yielding results within 1 percent H_2O 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°C (2°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), alternate methods, subject to the approval of the Control Agency's Authorized Representative, 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.

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 particulate matter.

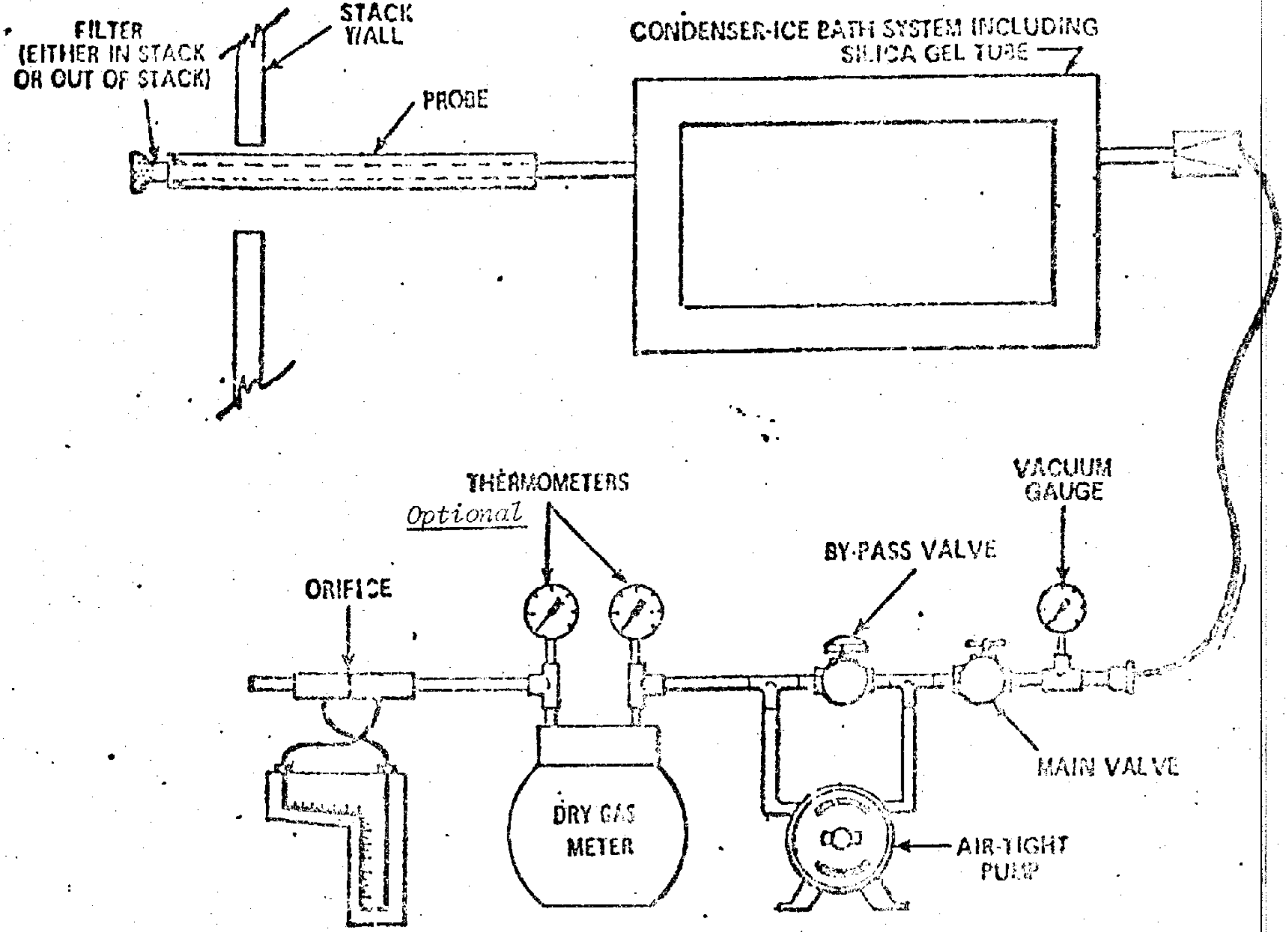

Figure 4-1. Moisture sampling train.

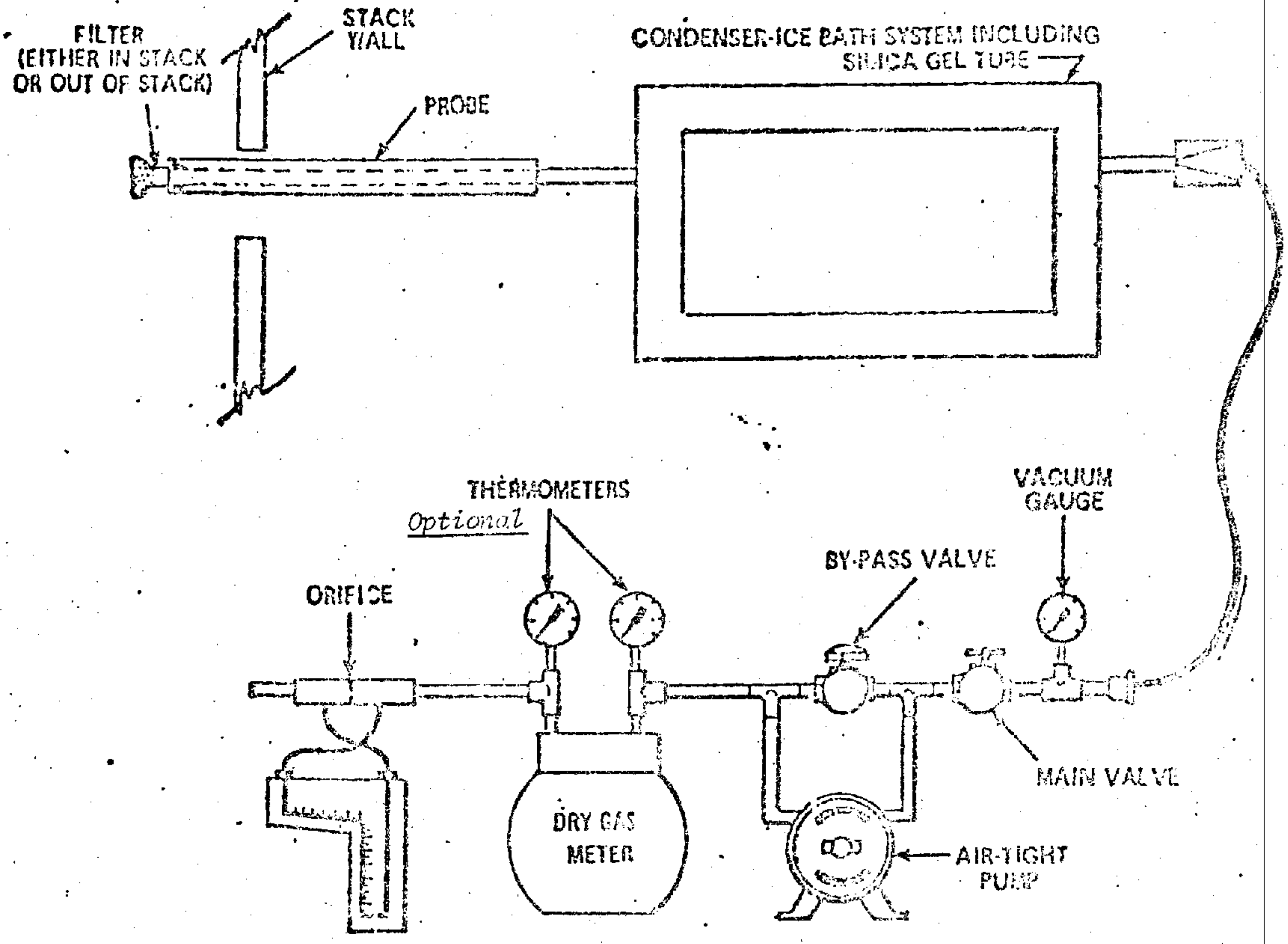

Figure 4-1. Moisture sampling train.

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Control Agency's Authorized Representative.

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 Control Agency's Authorized Representative.

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^{o}C (350^{o}F) for 2 hours. New silica gel may be used as received. A thermometer, capable of measuring temperature to within 1^{o}C (2^{o}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 Control Agency's Authorized Representative) 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°C (68°F), and determining the weight gain.

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

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°C (5.4°F), dry gas meter capable of measuring

Alternatively, any system may be used (subject to the approval of the Control Agency's Authorized Representative) 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 $20^{\circ}C$ ($68^{\circ}F$), 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 $3^{\circ}C$ ($5.4^{\circ}F$), 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 Control Agency's Authorized Representative.

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 Control Agency's Authorized Representative, 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 Control Agency's Authorized Representative. 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 and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 Unless otherwise specified by the Control Agency's Authorized Representative, 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 Control Agency's Authorized Representative. 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^3/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°C (248°F), to prevent water condensation ahead of the condenser; allow time for the temperature to stabilize. Place crushed ice in the ice bath container. It is required that a leak check be performed before and after each test 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^3/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 Control Agency's Authorized Representative. For each run, record the

FIGURE 4.2

Example Data Sheet for Moisture Determination

State of California
AIR RESOURCES BOARD

WATER VAPOR CALCULATIONS

Standard Conditions 68 °F and 29.92 in. Hg

Ambient Condtions ___ °F and ______ in. Hg

Time	Gas Volume Through Meter (V_m), Ft^3	Impinger Temp. (T_i), °F	Meter Temp. (T_m), °F	Orifice Pressure (ΔH), in. H_2O	Volume of Water Collected in Impinger (V_{l_c}), ml
					Final
					Initial
					Net (V_{l_c})

Assume 1 gram $H_2O \approx$ 1 ml H_2O

A. Gas Volume Metered $(V_{m_{std}})$

$$P_m = P_{bar} + (\Delta H/13.6) = (\qquad) + \frac{(\qquad)}{13.6} = \underline{\qquad\qquad} \text{ in. Hg}$$

$$V_{m_{std}} = \frac{528\ ^\circ R}{29.92 \text{ in. Hg}} \cdot \frac{V_m P_m}{T_m} = (17.64)\,\frac{(\qquad)(\qquad)}{(\qquad)} = \underline{\qquad\qquad} \text{ SCF}$$

B. Volume of Water Collected $(V_{w_{std}})$

$$V_{w_{std}} = \left(0.04707 \frac{Ft^3}{ml}\right)(V_{l_c}) = (0.04707)(\qquad) = \underline{\qquad\qquad} \text{ SCF}$$

C. Moisture Content in Stack Gas (Bw) in Percent

$$Bw = \frac{B}{A + B} \times 100 = \frac{(\qquad)}{(\qquad)} \times 100 = \underline{\qquad\qquad}$$

D. If calculated moisture content (C) is greater than at saturation temperature (e.g. 212°F or below) use the table for moisture content.

% OF H_2O AT SATURATION

TEMP. °F	% H_2O	TEMP. °F	% H_2O	TEMP. °F	% H_2O
50	1.2	130	15.1	180	51.3
60	1.7	140	19.7	185	57.0
70	2.5	150	25.3	190	63.6
80	3.5	155	28.7	195	70.6
90	4.8	160	32.5	200	76.6
100	6.5	165	36.4	205	87.0
110	8.7	170	40.3	210	93.2
120	11.5	175	45.7	212	100.0

FIGURE 4.2

Example Data Sheet for Moisture Determination

State of California
AIR RESOURCES BOARD

WATER VAPOR CALCULATIONS

Standard Conditions 68 °F and 29.92 in. Hg

Ambient Condtions ___ °F and ______ in. Hg

Time	Gas Volume Through Meter (V_m), Ft^3	Impinger Temp. (T_i), °F	Meter Temp. (T_m), °F	Orifice Pressure (ΔH), in. H_2O	Volume of Water Collected in Impinger (V_{1c}), ml
					Final
					Initial
					Net (V_{1c})

Assume 1 gram H_2O ≈ 1 ml H_2O

A. Gas Volume Metered (V_{mstd})

$$P_{ma} = P_{bar} + (\Delta H/13.6) = (\qquad) + \frac{(\qquad)}{13.6} = \underline{\qquad\qquad} \text{ in. Hg}$$

$$V_{mstd} = \frac{528\ °R}{29.92 \text{ in. Hg}} \cdot \frac{V_m\, P_{ma}}{T_m} = (17.64)\ \frac{(\qquad)(\qquad)}{(\qquad)} = \underline{\qquad\qquad} \text{ SCF}$$

B. Volume of Water Collected (V_{wstd})

$$V_{wstd} = \left(0.04707\ \frac{Ft^3}{ml}\right)(V_{1c}) = (0.04707)\ (\qquad) = \underline{\qquad\qquad} \text{ SCF}$$

C. Moisture Content in Stack Gas (Bw) in Percent

$$Bw = \frac{B}{A + B} \times 100 = \frac{(\qquad)}{(\qquad)} \times 100 = \underline{\qquad\qquad}$$

D. If calculated moisture content (C) is greater than at saturation temperature (e.g. 212°F or below) use the table for moisture content.

% OF H_2O AT SATURATION

TEMP. °F	% H_2O	TEMP. °F	% H_2O	TEMP. °F	% H_2O
50	1.2	130	15.1	180	51.1
60	1.7	140	19.7	185	57.0
70	2.5	150	25.3	190	63.0
80	3.5	155	28.7	195	70.4
90	4.8	160	32.5	200	76.8
100	6.5	165	38.4	205	87.0
110	8.7	170	40.3	210	93.2
120	11.5	175	45.7	212	100.0

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 than 20°C (68°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 and calculate the moisture percentage, as described in 2.3 below.

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.

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^3)/(g-mole) (K°) for metric units and 21.85 (in Hg) (ft^3)/(lb-mole) (°R) for English units.

T_m = Absolute temperature at meter. °K (°R).

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

V_m = Dry gas volume measured by the dry gas meter, dcm (dcf).

ΔV_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 plus impinger, g.

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.

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^3)/(g-mole) (K^o) for metric units and 21.85 (in Hg) (ft^3)/(lb-mole) (^oR) for English units.

T_m = Absolute temperature at meter. ^oK (^oR).

T_{std} = Standard absolute temperature, 293^o K (528^oR).

V_m = Dry gas volume measured by the dry gas meter, dcm (dcf).

ΔV_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 plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

P_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

2.3.2 Volume of water vapor condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\, p_w\, RT_{std}}{P_{std}\, M_w}$$

$$= K_1\, (V_f - V_i)$$

Equation 4-1

where: K_1 = 0.001333 m^3/ml for metric units

= 0.04707 ft^3/ml for English units

2.3.3 Volume of water vapor collected in silica gel.

$$V_{wsg(std)} = \frac{(W_f - W_i)\, RT_{std}}{P_{std}\, M_w}$$

$$= K_2\, (W_f - W_i)$$

Equation 4-2

where: K_2 = 0.001335 m^3/g for metric units

= 0.04715 ft^3/g for English units

2.3.4 Sample gas volume.

$$V_{m(std)} = V_m\, Y\, \frac{(P_m)\,(T_{std})}{(P_{std})\,(T_m)}$$

$$= K_3 Y \left(\frac{V_m P_m}{T_m}\right)$$

Equation 4-3

where: K_3 = 0.3858 ^{o}K/mm Hg for metric units

17.65 ^{o}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

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

Equation 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 ΔV_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 or 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.

2.3.5 Moisture Content

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

Equation 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 ΔV_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 or 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 midget 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 percent 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 plug before turning off the pump.

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 4-4.

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.

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 plug before turning off the pump.

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 4-4.

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.

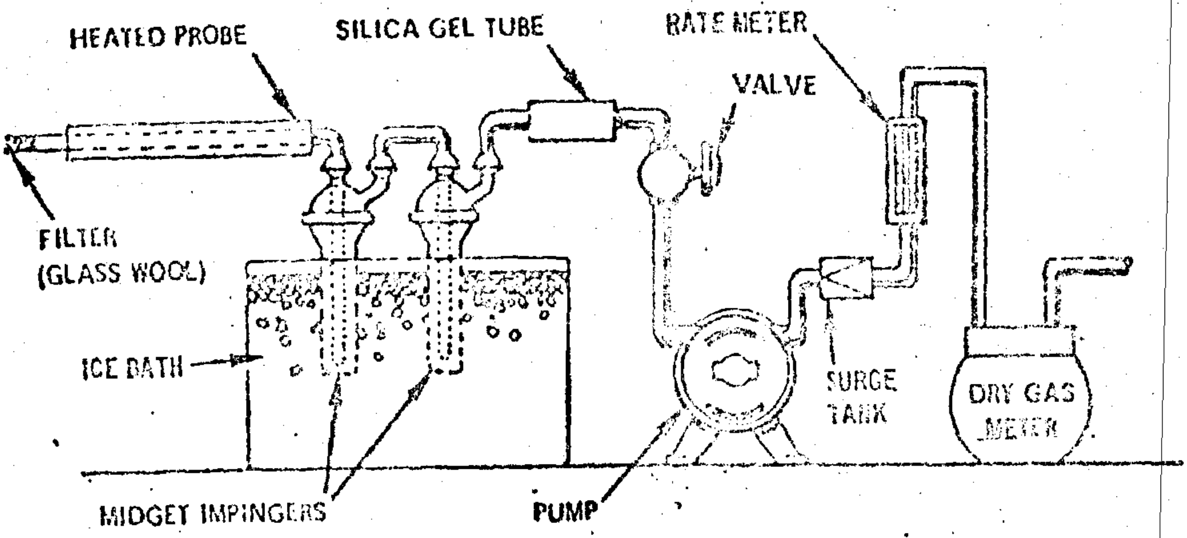

Figure 4.3 Moisture-sampling train - approximation method.

LOCATION ______________________ COMMENTS

TEST ______________________

DATE ______________________

OPERATOR ______________________

BAROMETRIC PRESSURE ______________________

CLOCK TIME	GAS VOLUME THROUGH METER, (Vm), m^3 (ft^3)	RATE METER SETTING m^3/min. (ft^3/min.)	METER TEMPERATURE, °C (°F)

Figure 4.4 Field moisture determination - approximation method.

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) ($^{\circ}$K) for metric units and 21.85 (in Hg) (ft^3)/lb-mole ($^{\circ}$R) for English units

T_m = Absolute temperature at meter, ^{0} ($^{\circ}$R).

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

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

Y = Dry gas meter calibration factor.

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) ($^{\circ}$K) for metric units and 21.85 (in Hg) (ft^3)/lb-mole ($^{\circ}$R) for English units

T_m = Absolute temperature at meter, $^{\circ}$ ($^{\circ}$R).

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

ρ_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.

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w RT_{(std)}}{P_{std} M_w}$$

$$= K_1 (V_f - V_i)$$

Equation 4-5

where: K_1 = 0.001333 m^3/ml for metric units

= 0.04707 ft^3/ml for English units

3.3.3 Gas Volume

$$V_m (std) = V_m \left(\frac{P_m}{P_{std}}\right) \left(\frac{T_{std}}{T_m}\right)$$

$$= K_2 Y \frac{V_m P_m}{T_m}$$

Equation 4-6

where: K_2 = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in. Hg for English units

3.3.4 Approximate moisture content.

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

$$= \frac{V_{wc}}{V_{wc(std)} + V_{m(std)}} + (0.025)$$

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

5. Bibliography

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2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co., Los Angeles, CA. Bulletin WP-50. 1968.

METHOD 5 - DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

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

Since the definition of particulate matter is not consistent in all rules, the particulate matter catch should be itemized by weight as follows: (1) Filter Catch, (2) Probe Catch, (3) Impinger Catch, and (4) Solvent Extract to allow adjustment of the particulate matter determination to be consistent with the applicable regulation.

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 Section 7); 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 Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be $\leq 30^{0}$ 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 Control Agency's Authorized Representative. 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 Control Agency's Authorized Representative.

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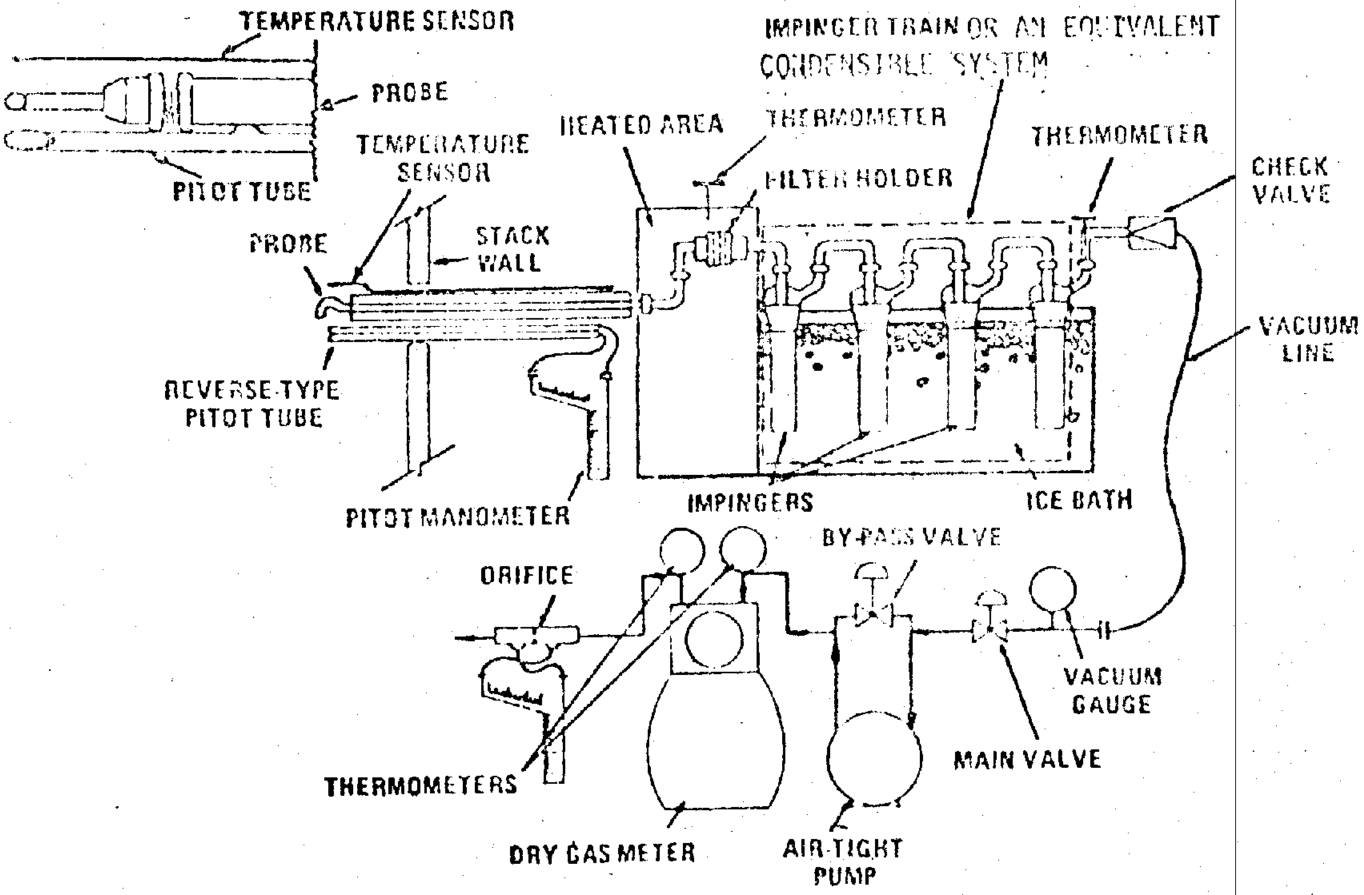

Figure 5-1 Particulate Sampling Train

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°C (248±25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Control Agency's Authorized Representative for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F); quartz liners shall be used for temperatures between 480

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

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

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

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[1] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

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 (P) 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 Control Agency's Authorized Representative. 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°C (248 ± 25°F), or such other temperature as specified by an applicable subpart of the standards or approved by the Control Agency's Authorized Representative for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C

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2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 ± 14^{o}C (248 ± 25^{o}F), or such other temperature as specified by an applicable subpart of the standards or approved by the Control Agency's Authorized Representative 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^{o}C

($5.4^{o}F$) 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 Impinger train. The following system shall be used to determine the stack gas moisture content and condensibles: 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 impinger train) may be used, subject ot the approval of the Control Agency's Authorized Representative. 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 $1^{o}C$ ($2^{o}F$) 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 impinger train, each to within 1 ml or 1 g may be used, subject to the approval of the Control Agency's Authorized Representative. Acceptable means are to measure the condensed water either gravimetrical or volumetrically and to measure the moisture leaving the impinger train by: (1) monitoring the temperature and pressure at the exit of the impinger train 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^{o}C (68^{o}F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the impinger train, it is recommended that silica gel (or equivalent) still be used between the impinger 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 particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be

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NOTE: If a determination of particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual 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 $3^{o}C$ ($5.4^{o}F$), dry gas meter capable of measuring volume to within 2 percent, and related equiment, 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 Control Agency's Authorized Representative. 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 APTD-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 Control Agency's Authorized Representative.)

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.

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2.2 Sample Recovery. The following items are needed:

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

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

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

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Control Agency's Authorized Representative.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1g. 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. Air-tight 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 polyethlene, 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.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1g. 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.

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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 ($\leq$ 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. Test data from the supplier's quality control program are sufficient for this purpose.

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

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

3.1.4 Crushed Ice.

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

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 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.

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

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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 Control Agency's Authorized Representative.

4. Procedure

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

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

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 its 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 $20 \pm 5.6^{\circ}C$ ($68 \pm 10^{\circ}F$) 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 Control Agency's Authorized Representative), the filters may be oven dried at $105^{\circ}C$ ($220^{\circ}F$) 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 Control Agency's Authorized Representative.

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 Control Agency's Authorized Representative. 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 containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

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

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 Control Agency's Authorized Representative. 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 alternative 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 Control Agency's Authorized Representative), 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 approximately 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 Control Agency's Authorized Representative'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.

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

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

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

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Control Agency's Authorized Representative, 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 required. 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 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 Control Agency's Authorized Representative, 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.

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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-cehck at about 25 mm Hg (1 in Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass 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^3/min (0.02 cfm) or 4 percent 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.

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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 not greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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

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.

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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 (Note: During the period before sampling begins point the nozzle downstream. Rotate the nozzle upstream immediately before the sampling pump is turned on.) 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 are taken to compensate for the deviations. (See Citation 7 in Section 7.)

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 Control Agency's Authorized Representative, 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 less than $20^{O}C$ ($68^{O}F$) 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 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 Control Agency's Authorized Representative, 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.

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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 Control Agency's Authorized Representative.

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 Control Agency's Authorized Representative 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 Control Agency's Authorized Representative 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.

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.

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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 from 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 Control Agency's Authorized Representative and shall be used when specified by the Control Agency's Authorized Representative; in these cases, save a water blank and follow the Control Agency's Authorized Representative'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.

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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 in 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 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 be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

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.

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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. (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.

4.2.1 Determination of the Particulate Concentration

The particulate matter concentration is determined by isokinetically aspirating a measured volume of the stack gas, catching the particulate in a filter, in the probe, connecting tubing, and in the impingers, and dividing the weight of the particulate catch by the volume of gas.

For the APCD rules, matter that is liquid at standard temperature must be included. This liquid matter is assumed to pass as a gas through the filter and to then condense in the impinger water. The weight of this liquid particulate is determined by solvent extraction using methylene chloride followed by an aqueous phase extraction. Caution must therefore be used not to let any acetone or other non-water rinse enter the impinger water.

For the APCD rules, the combined weight of the particulate matter caught in the probe, the filter and the impingers is used in the determination of particulate matter concentration. For some rules only the combined weight of the particulate matter caught in the probe and filter is used in the determination. Accordingly, it is advisable to report the weight of the impinger catch separately so that both the APCD and the ARB determinations can be made. The total particulate matter catch may be itemized by weight as follows: (1) Filter Catch, (2) Probe Catch, (3) Impinger Catch, and (4) Solvent Extract.

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:

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 methylene chloride followed by an aqueous phase extraction. Caution must therefore be used not to let any acetone or other non-water rinse enter the impinger water.

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

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Control Agency's Authorized Representative, 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.

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 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 identifed.

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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.

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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. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. 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 0.00057 m^3/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^3/min (0.02 cfm).

After each field use, the calibration of the metering systems 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 calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Control Agency's Authorized Representative.

Note - 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 according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

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

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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.

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_a = Acetone blank residue concentrations, mg/g.

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^3/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 "ith" component change ($i = 1, 2, 3, \ldots n$), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check m^3/min (cfm).

m_n = Total amount of particulate matter collected, mg.

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

m_a = Mass of residue of acetone after evaporation, mg.

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

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

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

R = Ideal gas constant 0.06236 mm Hg-m^3/^oK-g-mole (21.85 in Hg-ft^3/^oR-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), ^oK (^oR). Note: T_m will depend on type of meter used and sampling configuration.

T_s = Absolute average stack gas temperature (see Figure 5-2), ^oK (^oR).

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^3/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 "ith" component change (i = 1, 2, 3, ...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check m^3/min (cfm).

m_n = Total amount of particulate matter collected, mg.

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

m_a = Mass of residue of acetone after evaporation, mg.

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

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

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

R = Ideal gas constant 0.06236 mm Hg-m^3/°K-g-mole (21.85 in Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R). Note: T_m will depend on type of meter used and sampling configuration.

T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).

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

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

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

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

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in H_2O).

p_a = Density of acetone, mg/ml (see label on bottle).

p_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

0 = Total sampling time, min.

0_1 = Sampling time interval, from the beginning of a run until the first component change, min.

0_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

0_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

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

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

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

Equation 5-1

where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858^{o}K/\text{mm Hg for metric units.}$$

$= 17.64^{o}R/\text{in Hg}$ for English units.

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

0_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

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

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

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

Equation 5-1

where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858^{o}\text{K/mm Hg for metric units.}$$

$$= 17.64^{o}\text{R/in Hg for English units.}$$

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

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

$$V_m - (L_p - L_a)0$$

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

$$V_m - (L_i - L_a)0_1 - \sum_{i=2}^{n} (L_i - L_a)0 - (L_p - L_a)0_p$$

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

6.4 Volume of water vapor.

$$V_{w(std)} = V_{1c} \frac{p_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c}$$

Equation 5-2

where:

K_2 = 0.001333 m^3/ml for metric units.

= 0.04707 $ft^3 ml$ for English units.

6.5 Moisture Content.

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

Equation 5-3

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

6.6 Acetone Blank Concentrations.

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

Equation 5-4

6.7 Acetone Wash Blank.

$$W_a = C_a \, V_{aw} \, \rho_a$$

Equation 5-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). Note - Refer to Section 4.1.5 to assist in calculations of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$C_s = (0.001 \text{ g/mg}) \, (m_n / V_{m(std)})$$

Equation 5-6

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

6.6 Acetone Blank Concentrations.

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

Equation 5-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} p_a$$

Equation 5-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). Note - Refer to Section 4.1.5 to assist in calculations of results involving two or more filter assemblies or two or more sampling trains.

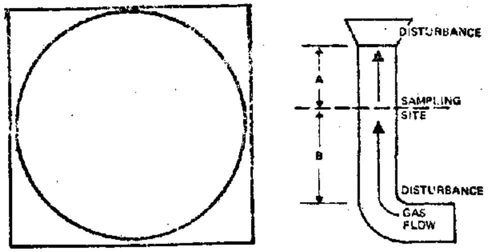
6.9 Particulate Concentration.

$$C_s = (0.001 \text{ g/mg}) (m_n/V_{m(std)})$$

Equation 5-6

PARTICULATE FIELD DATA

SCHEMATIC OF STACK



CROSS SECTION

PLANT ______

DATE ______

LOCATION ______

OPERATOR ______

STACK NO. ______

RUN NO. ______

SAMPLE BOX NO. ______

METER BOX NO. ______

AMBIENT TEMPERATURE ______

BAROMETRIC PRESSURE ______

ASSUMED MOISTURE, % ______

PROBE LENGTH, in. ______

NOZZLE DIAMETER, in. ______

STACK DIAMETER, in. ______

PROBE HEATER SETTING ______

HEATER BOX SETTING ______

METER $\Delta H_@$ ______

C FACTOR ______

PROCESS WEIGHT RATE ______

WEIGHT OF PARTICULATE COLLECTED, mg

SAMPLE	FILTER	PROBE WASH
FINAL WEIGHT		
TARE WEIGHT		
WEIGHT GAIN		
	TOTAL	

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (in. H_2O)	STACK TEMPERATURE (T_S), °F	VELOCITY HEAD (ΔP_S)	($\sqrt{\Delta P_S}$)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH) in., H_2O		GAS SAMPLE VOLUME (V_m), ft³	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE °F	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER °F	PUMP VACUUM in. Hg gauge	VELOCITY fps
						ACTUAL	DESIRED		INLET ($T_{m_{IN}}$), °F	OUTLET ($T_{m_{OUT}}$), °F				
TOTAL														
AVERAGE				☒										

VOLUME OF LIQUID WATER COLLECTED	IMPINGER VOLUME ml 1	2	3	4	SILICA GEL WEIGHT, g
FINAL					
INITIAL					
LIQUID COLLECTED					
TOTAL VOLUME COLLECTED					

ORSAT MEASUREMENT	TIME	CO_2	O_2	CO	N_2
1					
2					
3					
4					

COMMENTS:

FIGURE 5-2 PARTICULATE FIELD DATA

6.10 Conversion Factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I = \frac{100\ T_s\ K_3 V_{lc} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)}{60\ \ 0 v_s P_s A_n}$$

Equation 5-7

where:

K_3 = 0.003454 mm Hg - m^3/ml - °K for metric units.

= 0.002669 in Hg - ft^3/ml - °R for English units.

6.11.2 Calculation from Intermediate Values

$$I = \frac{T_s V_{m(std)}\ P_{std}\ 100}{T_{std} V_s\ 0\ A_n P_s 60\ (1 - B_{ws})}$$

$$= K_4\ \frac{T_s V_{m(std)}}{P_s V_s A_n 0\ (1 - B_{ws})}$$

Equation 5-8

where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

6.10 Conversion Factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

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Equation 5-7

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$$= K_4\ \frac{T_s V_{m(std)}}{P_s V_s A_n 0\ (1 - B_{ws})}$$

Equation 5-8

where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

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 (1g/ml).

$$\frac{\text{INCREASE, g}}{1\ \text{g/ml}} = \text{VOLUME WATER, ml}$$

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 (1g/ml).

$$\frac{\text{INCREASE, g}}{1\ \text{g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

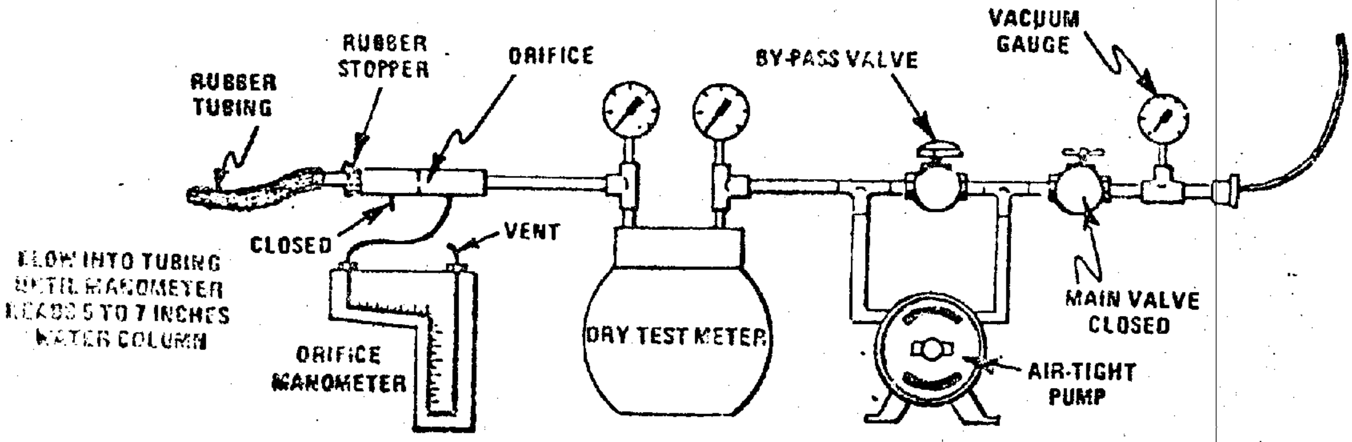

Figure 5-4. Leak check of meter box.

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3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March, 1972.

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5. Smith, W.S., et al. Stack Gas Sampling Improved and Simplified with New Equipment. APCA Paper No. 67-119. 1967.

6. Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. 1967.

7. Shigehara, R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News 2:4-11. October, 1974.

8. Vollaro, R.F. A Survey of Commercially Available Instrumentation For the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November, 1976 (unpublished paper).

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METHOD 6 - DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

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

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

Possible interferents are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO_2 analysis. When samples are being taken from a gas stream with high concentrations of very 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_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods subject to the approval of the Control Agency's Authorized Representative, are required.

2. Apparatus

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

bubbler, and hence do not affect the SO_2 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_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods subject to the approval of the Control Agency's Authorized Representative, are required.

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

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

2.1.1 Probe: Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the Control Agency's Authorized Representative), 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.

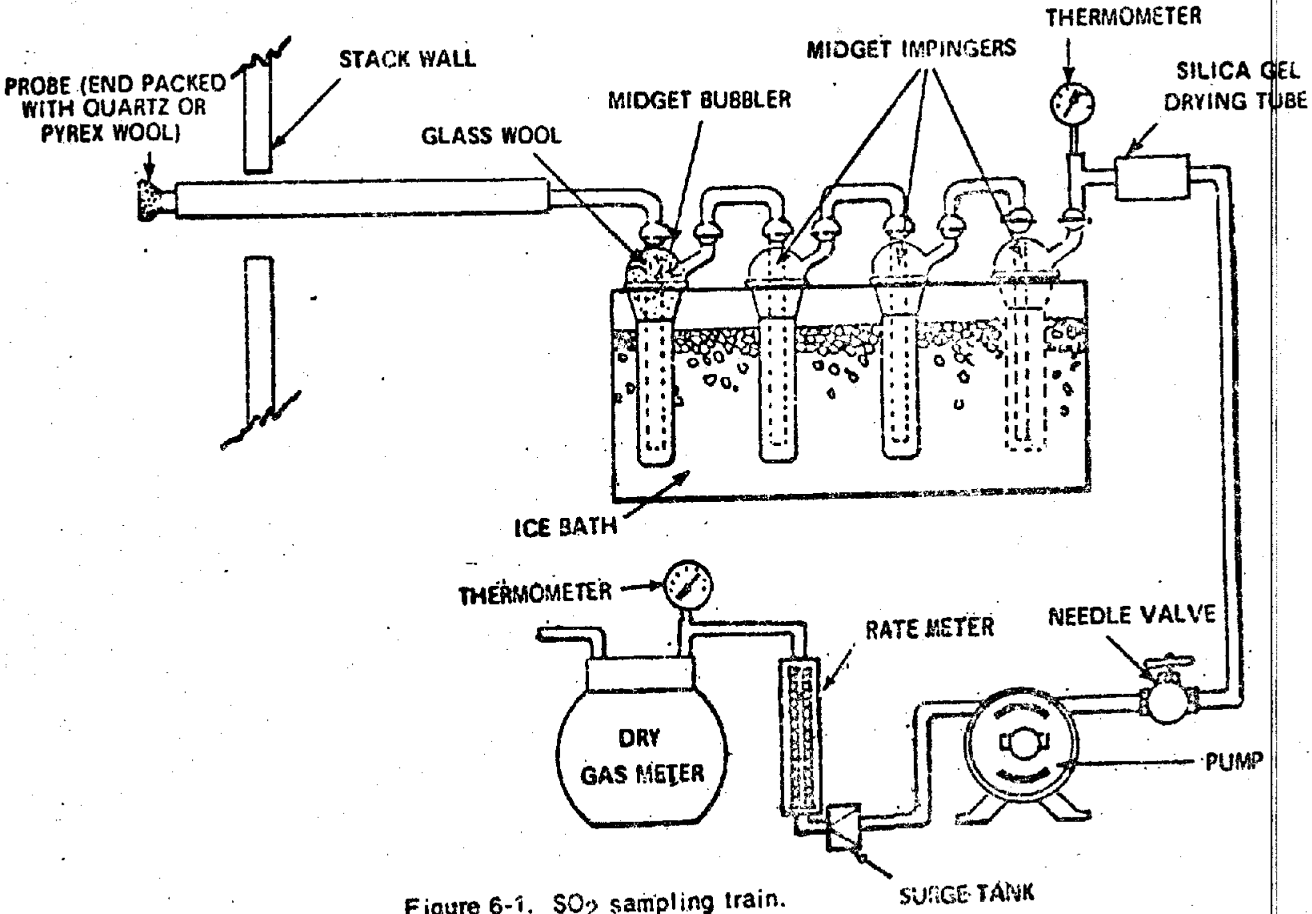

Figure 6-1. SO_2 sampling train.

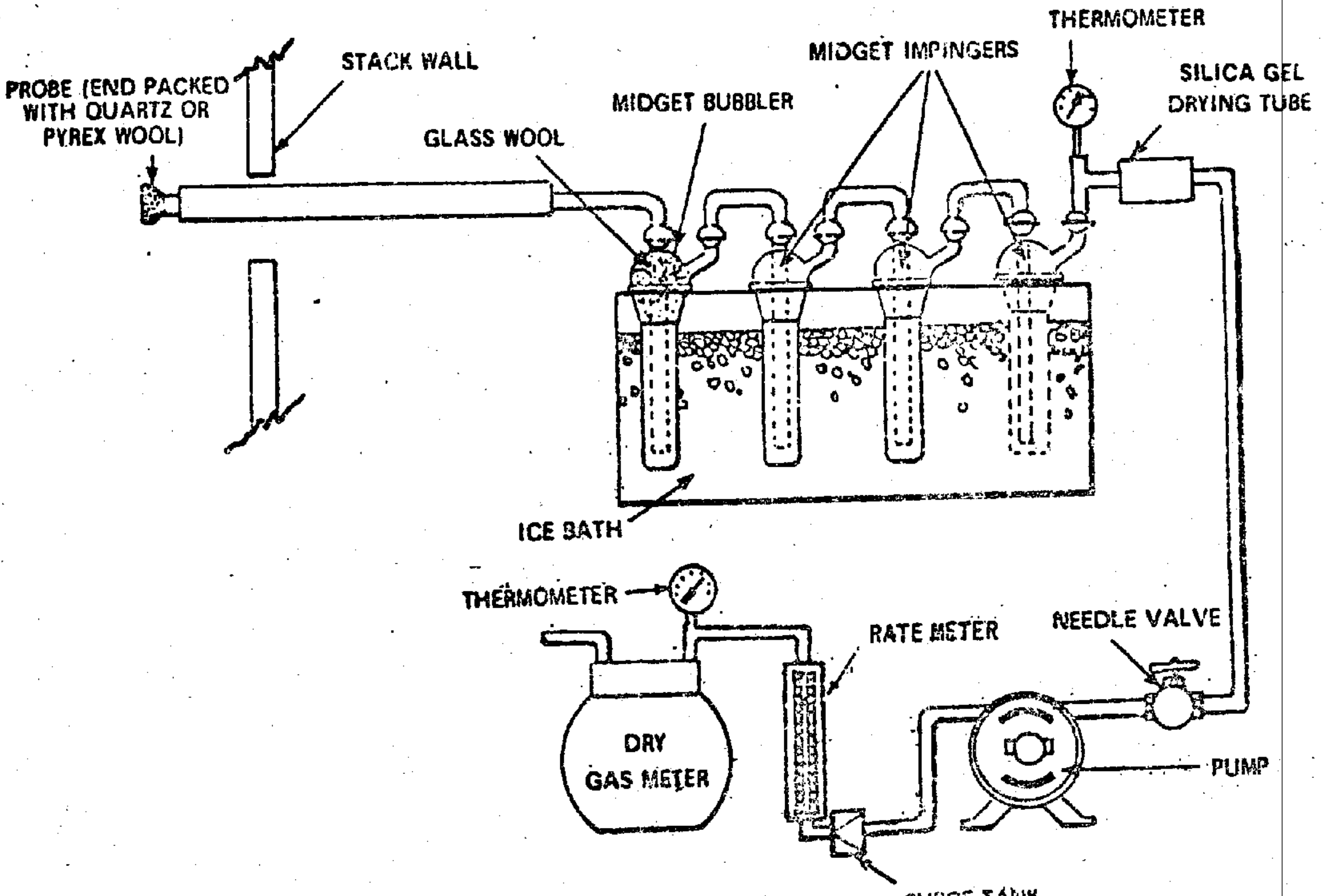

Figure 6-1. SO_2 sampling train.

Other collection absorbers and flow rates may be used, but are subject to the approval of the Control Agency's Authorized Representative. Also, collection efficiency must be shown to be at least 90 percent for each test run and must be documented in the report.

If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

2.1.3 Glass Wool: Borosilicate or quartz.

2.1.4 Stopcock Grease: Acetone-insoluble, heat-stable 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^oC (2^oF).

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^oC (350^oF) 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 Control Agency's Authorized Representative.

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

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

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

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

2.1.11 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute other types of desiccants (equivalent or better) may be used, subject to approval of the Control Agency's Authorized Representative.

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.

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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 evaluation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) for 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 Sampling 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 D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 Percent: Mix 80 ml of isopropanol with 20 ml of deionized, distilled water. Check each lot of

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 D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

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

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

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

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

3.2 Sample Recovery.

3.2.1 Water: deionized, distilled as in 3.1.1.

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

3.3 Analysis

3.3.1 Water: Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 Percent.

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

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

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

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train: Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two

3.3 Analysis

3.3.1 Water: Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 Percent.

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

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

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

4. Procedure

4.1 Sampling.

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

4.1.2 Leak-check Procedure: After assembly at the test site, the sampling train must be leak-checked. A leak-check after each 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 proble 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 pubp 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 Hg (10 in. Hg) at the inlet to either the drying tube or the pump, 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 Control Agency's Authorized Representative. The procedure used in Method 5 is not suitable for diaphragm pumps.

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 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 Hg (10 in. Hg) at the inlet to either the drying tube or the pump, 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 Control Agency's Authorized Representative. The procedure used in Method 5 is not suitable for diaphragm pumps.

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°C (68°F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak check as in Section 4.1.2. (This leak check is mandatory.) If a leak is found, void the test run or, if appropriate, use procedures acceptable to the Control Agency's Authorized Representative to adjust the sample volume for leakage. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

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

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

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

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink 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.

(Note - Protect the 0.0100 N barium perchlorate solution from evaporation at all times.)

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

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 Control Agency's Authorized Representative, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink 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.

(Note - Protect the 0.0100 N barium perchlorate solution from evaporation at all times.)

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 or 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 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 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.

and (c) only two independent runs need be made. If the calibration factor does not deviate by more 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.

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 Nomeclature.

C_{SO_2} = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in Hg).

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

T_m = Average dry gas meter absolute temperature, ^{o}K (^{o}R).

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

V_s = 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 of 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.

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METHOD 7 - DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle: A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimeterically 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 Control Agency's Authorized Representative. The following equipment is used in sampling:

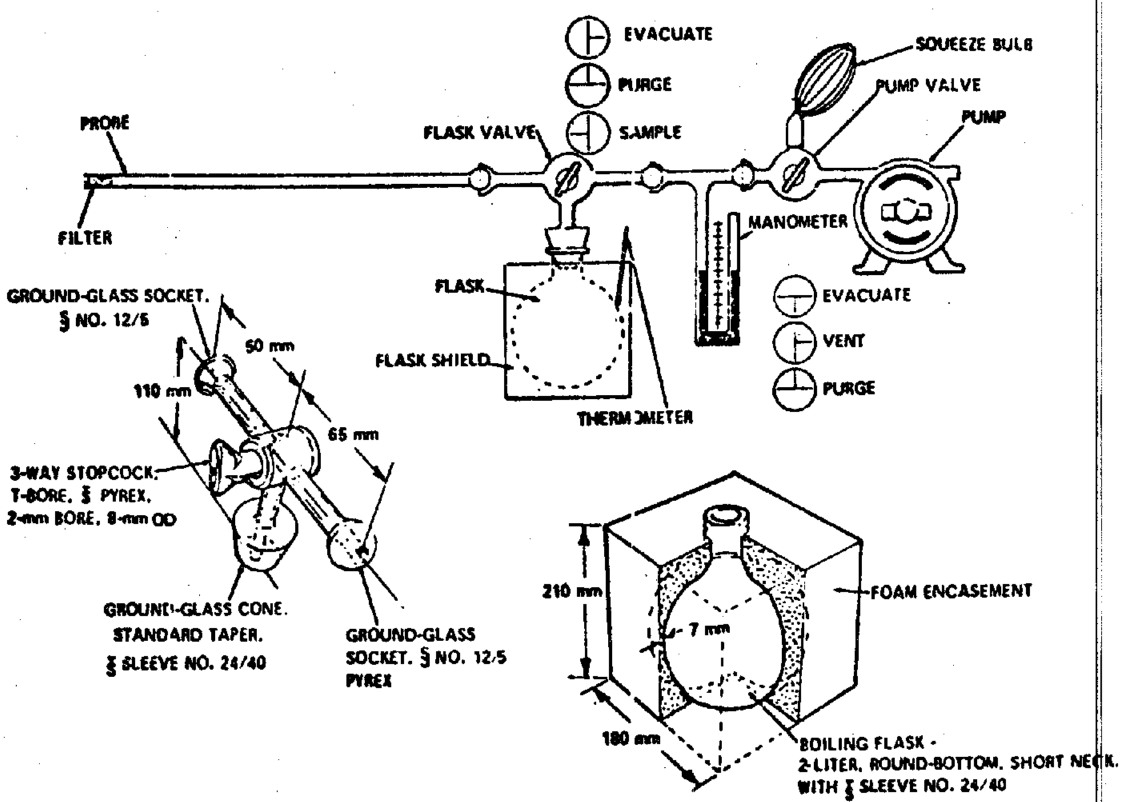

Figure 7-1. Sampling train, flask valve, and flask.

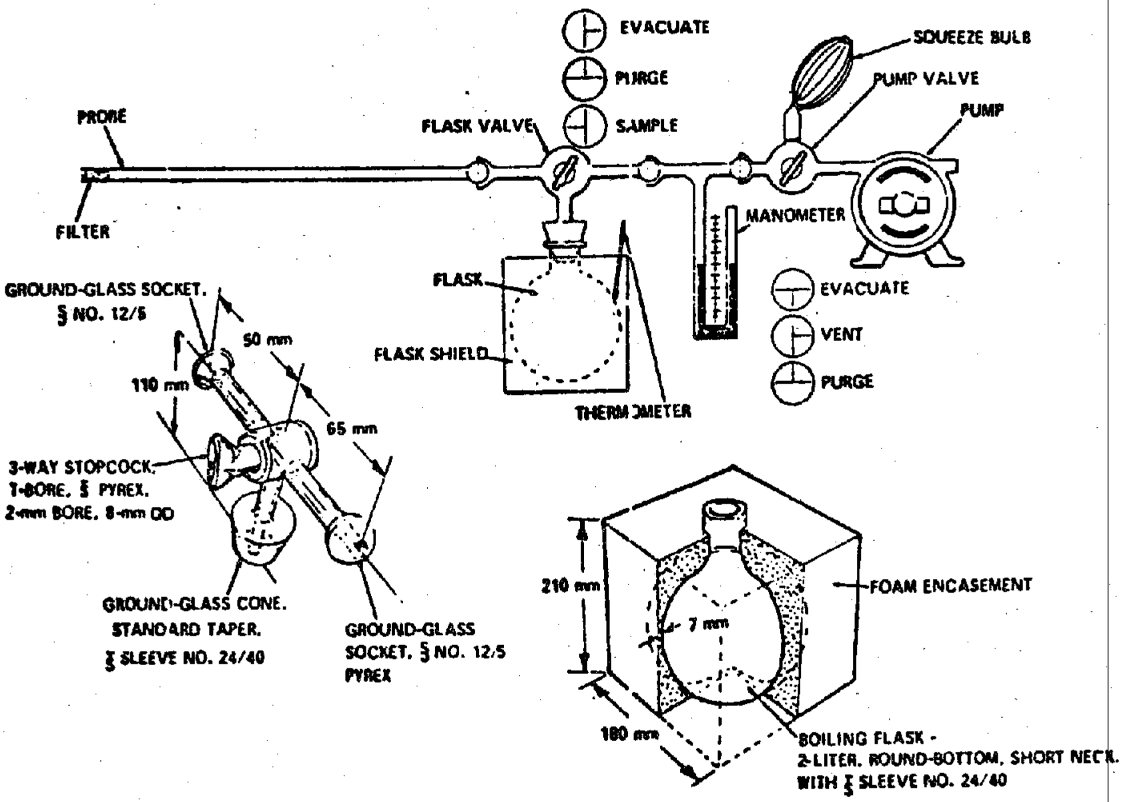

Figure 7-1. Sampling train, flask valve, and flask.

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

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

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

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

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

[1/] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

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 77 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.

2.1.6 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 77 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 Procelain Evaporting Dishes: 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallow-form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration (see Section 4.3).

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

2.3.4 Dropping Pipette or Dropper: Three required.

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

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

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

2.3.8 Spectrophotometer: To measure absorbance at 410 nm.

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

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

2.3.11 Analytical Balance: To measure to within 0.1 mg.

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

2.3.4 Dropping Pipette or Dropper: Three required.

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

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

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

2.3.8 Spectrophotometer: To measure absorbance at 410 nm.

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

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

2.3.11 Analytical Balance: To measure to within 0.1 mg.

3. Reagents

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

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

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

3.2.1 Sodium (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 D1193-74, Type 3. At the option of the analyst, the $KMNO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

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

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

3.3.2 Phenol: White solid.

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

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

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

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

3.3.7 Water: Deionized, distilled as in Section 3.2.2.

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

3.3.2 Phenol: White solid.

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

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

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

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

3.3.7 Water: Deionized, distilled as in Section 3.2.2.

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

4. Procedure

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_i), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask vave area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2), then oxygen shall 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 vave 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_1) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

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

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

4.3 Analysis: Note the level of the liquid in the 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 Control Agency's Authorized Representative, to correct the final results. Immediately prior to the analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the procelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml, or more, 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).

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If the sample contains solids these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Control Agency's Authorized Representative), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask, rinse the evaporating dish with three, approximately, 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 ug NO_2 standard (see Section 5.2.2).

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 ug NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination.

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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 ug 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 range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_2 working standard solution (1 ml = 100 ug 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 procelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

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

Equation 7-1

where:

K_c = Calibration factor

A_1 = Absorbance of the 100-ug NO_2 standard

A_2 = Absorbance of the 200-ug NO_2 standard

A_3 = Absorbance of the 300-ug NO_2 standard

A_4 = Absorbance of the 400-ug NO_2 standard

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.

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6. Calculation

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

6.1 Nomenclature

A = Absorbance of sample.

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

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

K_c = Spectrophotometer calibration factor.

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

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

P_i = Initial absolute pressure, 760 mm Hg (29.92 in. Hg).

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

T_f = Final absolute temperature of flask, ^oK (^oR).

T_i = Initial absolute temperature of flask, ^oK (^oR).

T_{std} = Standard absolute temperature, 293^oK (528^oR).

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.

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

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

Equation 7-2

where

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

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

6.3 Total ug NO_2 Per Sample.

$$m = 2K_c AF$$

Equation 7-3

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

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

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

Equation 7-4

where

K_2 = $10^3 \frac{\text{mg/m}^3}{\text{ug/ml}}$ for metric units

= $6.243 \times 10^{-5} \frac{\text{lb/scf}}{\text{ug/ml}}$ for English units

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

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

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

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

1. Principle and Applicability

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

1.2 Applicability: This method is applicable for the 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 (0.03×10^{-7} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m^3 (0.74×10^{-7} lb/ft^3) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentraton limit for sulfur dioxide in a 1.0 m^3 (35.3 ft^3) gas sample is about 12,500 mg/m^3 (7.7×10^{-4} lb/ft^3). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents are present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Control Agency's authorized representative, are required.

Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the Control Agency's authorized representative) 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_2SO_4 acid mist is not determined separately.

2. Apparatus

2.1 Sampling: A schematic of the sampling train used in this method is shown in Figure 8-1; it is 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.

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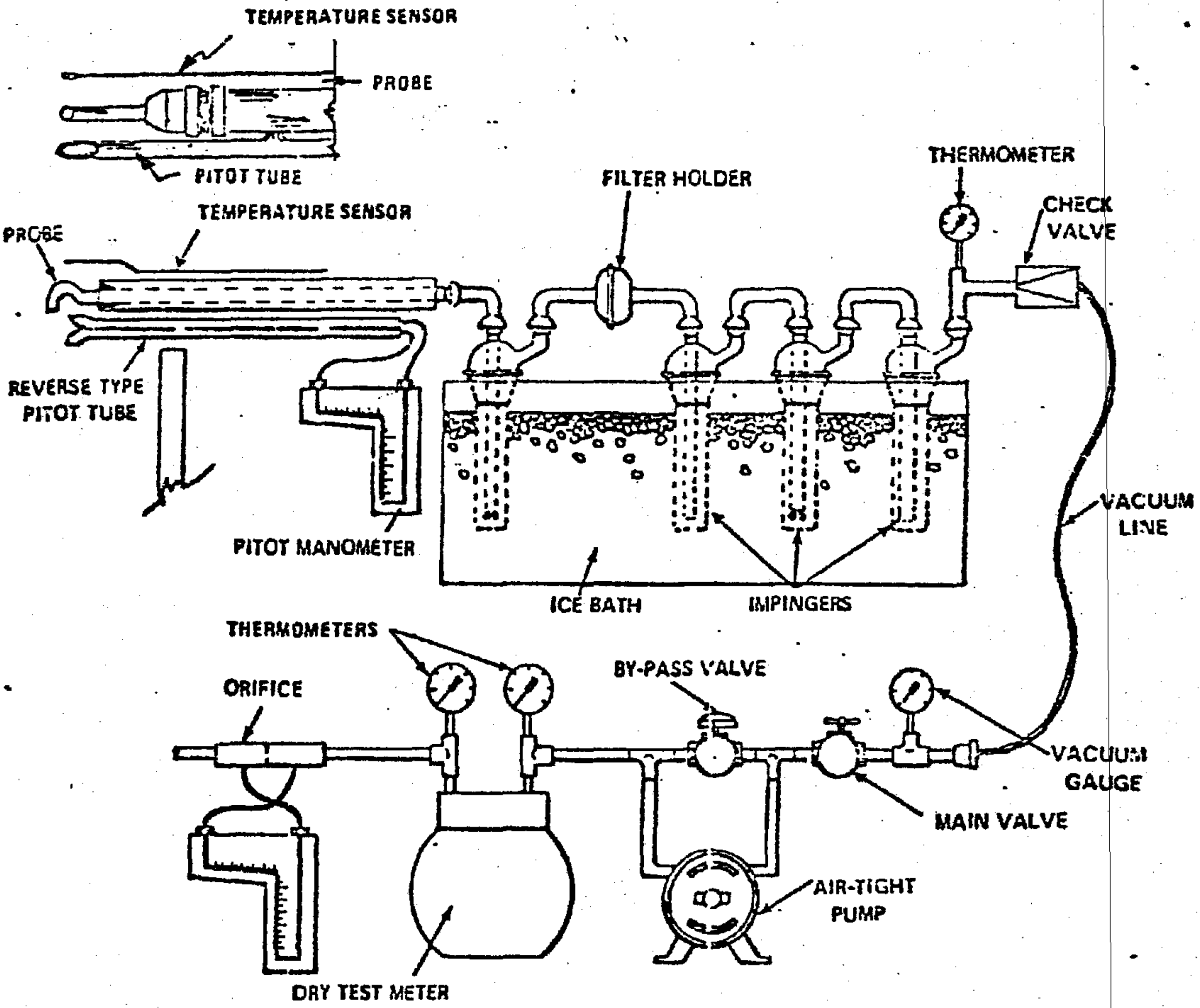

Figure 8-1. Sulfuric acid mist sampling train.

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

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

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

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

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

2.1.5 Filter Holder: Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials, e.g., Teflon or Viton, may be used subject to the approval of the Control Agency's authorized representative. The holder design shall provide a positive seal against leakage from the outside or around

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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 Control Agency's authorized representative. 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 Greenburn-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in.) ID glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Control Agency's authorized representative 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 $1^{o}C$ ($2^{o}F$).

2.2 Sample Recovery.

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

2.2.2 Graduated Cylinders: 250 ml, 1 liter. (Volumetric Flasks may also be used.)

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

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

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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 D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentratons 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 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. Peroxides may be removed from isopropanol by redistilling, or by passage through a column of activated alumina. However, reagent-grade isopropanol with suitably low peroxide levels is readily available from commercial sources; therefore, rejection of contaminated lots may be more efficient than following the peroxide removal procedure.

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

3.1.6 Crushed ice.

3.2 Sample Recovery.

3.2.1 Water: Same as 3.1.3.

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

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

3.1.6 Crushed ice.

3.2 Sample Recovery.

3.2.1 Water: Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent: Same as 3.1.4.

3.3 Analysis

3.3.1 Water: Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

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

3.3.4 Barium Perchlorate (0.0100 Normal): Dissolve 1.95 g of barium perchlorate trihydrate $[Ba(ClO_4)_2 \cdot 3H_2O]$ in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol; 1.22 g of barium chloride dihydrate $(BaCL_2 \cdot 2H_2O)$ may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

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

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

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 heaters hall 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."

4.1.5 Train Operation: Follow the basic procedure outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed $0.030 m^3$/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this

FIELD DATA

Run No. ____________

Location ____________

Date ____________

Operator ____________

Sample Box No. ____________

Meter Box No. ____________

<u>VERY IMPORTANT</u> - <u>FILL IN ALL BLANKS</u>

Read and record at the start of each test point.

Leak Test = Before ______ After ______

Pitot Tube Factor ____________

Ambient Temp °F ____________

Bar. Press."Hg ____________

Assumed Moisture % ____________

Heater Box Setting, °F ________

Probe Tip Dia., In. ________

Probe Length ____________

Probe Heater Setting ________

Point	Clock Time	Dry Gas Meter, CF	Pitot in. H_2O ΔP	Orifice ΔH in H_2O		Dry Gas Temp. °F		Pump Vacuum In. Hg Gauge	Impinger Temp °F	Stack Press In. Hg	Stack Temp °F
				Desired	Actual	Inlet	Outlet				

Figure 8[illegible]ield Data

FIELD DATA

Ambient Temp °F ______

Run No. ______

Bar. Press."Hg ______

Location ______

VERY IMPORTANT - FILL IN ALL BLANKS

Assumed Moisture % ______

Date ______

Read and record at the start of each test point.

Heater Box Setting, °F ______

Operator ______

Probe Tip Dia., In. ______

Leak Test = Before ______ After ______

Sample Box No. ______

Probe Length ______

Meter Box No. ______

Pitot Tube Factor ______

Probe Heater Setting ______

Point	Clock Time	Dry Gas Meter, CF	Pitot in. H_2O ΔP	Orifice ΔH in H_2O		Dry Gas Temp. °F		Pump Vacuum In. Hg Gauge	Impinger Temp °F	Stack Press In. Hg	Stack Temp °F
				Desired	Actual	Inlet	Outlet				

Figure 8 Field Data

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 outlind in Section 6.3 of Method 5. Immediately after component changes, conduct leak-checks per the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications).

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.

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 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 Control Agency's authorized representative, 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 thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

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

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.

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 prcent or 0.2 ml, whichever is greater.

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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 = 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_2) 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, g equivalents/liter.

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), ^{o}K (^{o}R).

T_s = Average absolute stack gas temperature (see Figure 8-2), ^{o}K (^{o}R).

T_{std} = Standard absolute temperature, $293^{\circ}K$ ($528^{\circ}R$).

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 measure 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 dioixde sample is contained, 250 ml or 1,000 ml, respectively.

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

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

Y = Dry gas meter calibration factor.

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

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent

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

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 measure 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 dioixde sample is contained, 250 ml or 1,000 ml, respectively.

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

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

Y = Dry gas meter calibration factor.

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

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent

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

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

$$V_{m(std)} = V_m Y \frac{P_{bar} + (\Delta H/13.6)}{P_{std}}$$

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

Equation 8-1

where:

K_1 = 0.3858 ^{o}K/mm Hg for metric units.
17.65 ^{o}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 effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

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

Equation 8-2

where

K_2 = 0.04904 g/milliequivalent for metric units.

= 1.081×10^{-4} lb/meq for English units.

6.6 Sulfur dioxide concentraton.

$$C_{SO_2} = K_3 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}}$$

Equation 8-3

where

K_3 = 0.03203 g/meq for metric units.

= 7.061×10^{-5} lb/meq for English units.

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 effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

$$C_{H_2SO_4} = K_2 N \frac{(V_t - V_{tb})\ (V_{soln}/V_a)}{V_m\ (std)}$$

Equation 8-2

where

K_2 = 0.04904 g/milliequivalent for metric units.

= 1.081×10^{-4} lb/meq for English units.

6.6 Sulfur dioxide concentraton.

$$C_{SO_2} = K_3\ N \frac{(V_t - V_{tb})\ (V_{soln}/V_a)}{V_m\ (std)}$$

Equation 8-3

where

K_3 = 0.03203 g/meq for metric units.

= 7.061×10^{-5} lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data

$$I = \frac{100\ T_s\ [K_4\ V_{1c} + V_m\ Y/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\ \theta\ v_s\ P_s\ A_n}$$

Equation 8-4

where

K_4 = 0.003464 mm Hg m^3/ml ^oK for metric units.

= 0.002676 in. Hg ft^3/ml ^oR for English units.

6.7.2 Calculation from intermediate values.

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

$$= K_5\ \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1 - B_{ws})}$$

Equation 8-5

where:

K_5 = 4.320 for metric units.

= 0.09450 for English units.

6.8 Acceptable Results. If≤90 percent I≤ 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may opt to accept the results. Use Citation 4 in the Bibliography of Method 5 to make judgements. Otherwise, reject the results and repeat the test.

7. Bibliography

1. Atmospheric Emissions from Sulfur Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution. Public Health Service Publication No. 999-AP-13. Cincinnati, Ohio. 1965.

2. Corbett, P.F. The Determination of SO_2 and SO_3 in Flue Gases. Journal of the Institute of Fuel. 24:237-243. 1961.

3. Martin, Robert M. Construction Details of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. Air Pollution Control Office Publication No. APTD-0581. April 1971.

4. Patton, W. F. and J.A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases. Journal of Air Pollution Control Association. 13:162. 1963.

5. Rom, J.J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March 1972.

6. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for Determination of Sulfur Dioxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Environmental Protection Agency. Research Triangle Park, N.C. EPA-650/4-74-024. December 1973.

7. Annual Book of ASTM Standards. Part 31; Water Atmospheric Analysis. pp. 40-42. American Society for Testing and Materials. Philadelphia, PA 1974.

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1. Atmospheric Emissions from Sulfur Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution. Public Health Service Publication No. 999-AP-13. Cincinnati, Ohio. 1965.

2. Corbett, P.F. The Determination of SO_2 and SO_3 in Flue Gases. Journal of the Institute of Fuel. 24:237-243. 1961.

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7. Annual Book of ASTM Standards. Part 31; Water Atmospheric Analysis. pp. 40-42. American Society for Testing and Materials. Philadelphia, PA 1974.

METHOD 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 nondispersive infrared analyzer (NDIR) or equivalent.

1.1 Applicability: This method is applicable for the determination of carbon monoxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The test procedure will indicate whether a continuous or an integrated sample is to be used.

2. Range and Sensitivity

2.1 Range: 0 to 1,000 ppm.

2.2 Sensitivity: Minimum detectable concentration is 20 ppm for a 0 to 1,000 ppm span.

3. Interferences

Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water

(H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. Precision and Accuracy

4.1 Precision: The precision of most NDIR analyzers is approximately ±2 percent of span.

4.2 Accuracy: The accuracy of most NDIR analyzers is approximately ±5 percent of span after calibration.

5. Apparatus

5.1 Continuous Sample (Figure 10-1).

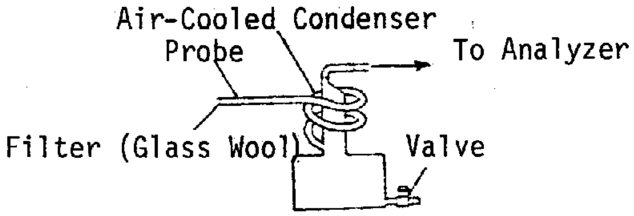

Figure 10-1. Continuous sampling train.

5.1.1 Probe: Stainless steel or sheathed borosilicate or quartz glass, equipped with a filter to remove particulate matter.

(H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. Precision and Accuracy

4.1 Precision: The precision of most NDIR analyzers is approximately ±2 percent of span.

4.2 Accuracy: The accuracy of most NDIR analyzers is approximately ±5 percent of span after calibration.

5. Apparatus

5.1 Continuous Sample (Figure 10-1).

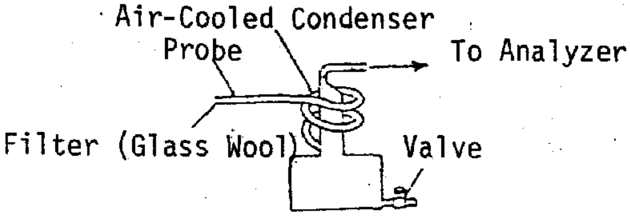

Figure 10-1. Continuous sampling train.

5.1.1 Probe: Stainless steel or sheathed borosilicate or quartz glass, equipped with a filter to remove particulate matter.

5.1.2 Air-cooled Condenser or Equivalent: To remove any excess moisture.

5.1.3 Sample Line: Line shall be made of Teflon, and if necessary, insulated and capable of being heated to a minimum of 120°C. If condensation is not a problem, sample line does not have to be heated. Alternatively, sample line made from other material (equivalent or better) may be used subject to the approval of the Control Agency's Authorized Representative.

5.2 Integrated sample (Figure 10-2).

5.2.1 Probe. Stainless steel or sheathed borosilicate or quartz 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.^{3}). 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.

5.2.8 Sample Line: (See Section 5.1.3).

5.3 Analysis (Figure 10-3)

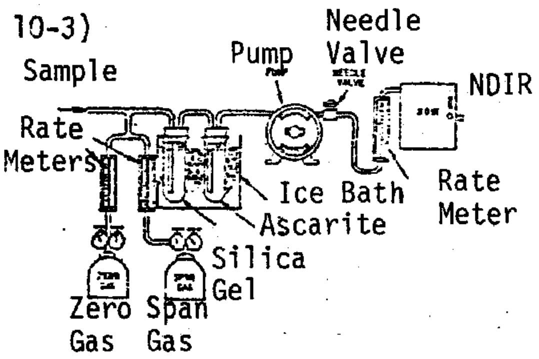

Figure 10-3. Analytical equipment

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 or Method 100.

5.3.2 Drying Tube: To contain approximately 200 g of silica gel. Acceptable alternatives would include the refrigeration system specified under Method 100 (Section 2.1.4) or other types of desiccants (equivalent or better), subject to the approval of the Control Agency's Authorized Representative.

5.3.3 Calibration Gas: Refer to paragraph 6.1.

5.3.4 Filter: As recommended by NDIR manufacturer.

5.3.5 CO_2 Removal Tube: To contain approximately 500 g of ascarite. Alternatively, other methods of CO_2 interference elimination (equivalent or better) may be used, subject to the approval of the Control Agency's Authorized Representative. Acceptable methods would be an analyzer with a filter or electronic signal conditioning to correct CO_2 interference.

5.3.6 Ice Water Bath: For ascarite and silica get tubes, if used.

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.

5.3.2 Drying Tube: To contain approximately 200 g of silica gel. Acceptable alternatives would include the refrigeration system specified under Method 100 (Section 2.1.4) or other types of desiccants (equivalent or better), subject to the approval of the Control Agency's Authorized Representative.

5.3.3 Calibration Gas: Refer to paragraph 6.1.

5.3.4 Filter: As recommended by NDIR manufacturer.

5.3.5 CO_2 Removal Tube: To contain approximately 500 g of ascarite. Alternatively, other methods of CO_2 interference elimination (equivalent or better) may be used, subject to the approval of the Control Agency's Authorized Representative. Acceptable methods would be an analyzer with a filter or electronic signal conditioning to correct CO_2 interference.

5.3.6 Ice Water Bath: For ascarite and silica get tubes, if used.

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

Zero Gas: Pure air or nitrogen with less than 1 ppm of CO.

Span Gas: The calibration gas shall be approximately 70-80 percent of the analyzer range but not more than 150 percent of the applicable source performance standard unless exceeded by the source. The expected maximum concentration to be measured should not be more than 90 percent of the analyzer range. The calibration gas shall be traceable to the National Bureau of Standards primary standard gas blend. Known concentration of CO in nitrogen (N_2) for instrument span, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.

6.2 Silica Gel: Indicating type, 6 to 16 mesh, dried at 175°C (350°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 probe 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 paragraphs 7.2 and 8.) CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 Integrated Sampling: Evacuate the flexible bag. Set up the equipment as shown in Figure 10-3 with the bag disconnected.

Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7. 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 probe 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 paragraphs 7.2 and 8.) CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 Integrated Sampling: Evacuate the flexible bag. Set up the equipment as shown in Figure 10-3 with the bag disconnected.

Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures, or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.2 CO Analysis: Assemble the apparatus as shown in Figure 10-3, calibrate the instrument, and perform other required operations as described in paragraph 8. Purge analyzer with N_2 prior to introduction of each sample. Direct the sample stream through the instrument for the test period, recording the readings. Check the zero and span again after the test to assure that any drift or malfunction is detected. Record the sample data on Table 10-1.

8. Calibration

Assemble the apparatus according to Figure 10-3. Generally an instrument requires a warm-up period before stability is obtained. Follow the manufacturer's instructions for specific procedure. Allow a minimum time of one hour for warm-up. During this time check the sample conditioning apparatus, i.e., filter, condenser, drying tube, and CO_2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen or zero grade air and the calibration gases.

9. Calculation - Concentration of Carbon Monoxide: Calculate the concentration of carbon monoxide in the stack using Equation 10-1.

$$C_{CO_{stack}} = C_{CO_{NDIR}} \quad (1-F_{CO_2})$$

Equation 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.

= 0 if CO_2 interference is eliminated by means other than CO_2 physical removal.

ADDENDA

A. Performance Specifications for NDIR Carbon Monoxide Analyzers

Range (minimum)	0-1000 ppm
Output (minimum)	0-10 mV
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 (maximum)	± 2% of full scale
Noise (maximum)	± 1% of full scale
Linearity (maximum deviation)	2% of full scale
Interference rejection ratio	CO_2 - 1000 to 1, H_2O - 500 to 1

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).

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Noise (maximum)	± 1% of full scale
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Interference rejection ratio	CO_2 - 1000 to 1, H_2O - 500 to 1

B. Definitions of Performance Specifications

Range - The minimum and maximum measurement limits.

Output Electrical signal which is proportional to the measurement; intended for connection to readout of 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.

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.

10. Bibliography

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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_2S) is collected from a source in a series of midget impingers and absorbed in pH 3.0 cadmium sulfate ($CdSO_4$) solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species.

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^3 (6 ppm). The maximum of the range is 740 mg/m^3 (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^3 is eliminated by the hydrogen peroxide solution. Thiols precipitate with hydrogen sulfide. In the absence of H_2S, only co-traces of thiols are collected. When methane- and ethane-thiols at a total level of 300 mg/m^3 are present in addition to H_2S, the results vary from 2 percent low at an H_2S concentration of 400 mg/m^3 to 14 percent high at an H_2S concentration of 100 mg/m^3. 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_2S was present. In the presence of the interferences cited in Section 3, the bias was positive at low H_2S concentrations and negative at higher concentrations. At 230 mg H_2S/m^3, the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

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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.

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5. Apparatus.

5.1 Sampling Apparatus.

5.1.1 Sampling Line. Six to 7 mm (1/4 in.) Teflon[1/] tubing to connect the sampling train to the sampling valve.

5.1.2 Impingers. Five midget 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 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°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Control Agency's Authorized Representative.

[1/]. Mention of trade names of specific products does not constitute endorsement by the Air Resources Board.

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 (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 $3^{0}C$ ($5.4^{0}F$). 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.

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.

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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 from 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 $0^{o}C$ ($32^{o}F$) to avoid condensation of C_3 or C_4 hydrocarbons.

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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 the best available grade.

6.1 Sampling.

6.1.1 Cadmium sulfate absorbing solution. Dissolve 41 g of $3CdSO_4 \cdot 8H_2O$ and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately 3/4 liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be 3±0.1. Add 10 drops of Dow-Corning Antifoam B. Shake well before use. If Antifoam B is not used, the alternate 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 $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

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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.

6.1 Sampling.

6.1.1 Cadmium sulfate absorbing solution. Dissolve 41 g of $3CdSO_4 \cdot 8H_2O$ and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately 3/4 liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be 3 ± 0.1. Add 10 drops of Dow-Corning Antifoam B. Shake well before use. If Antifoam B is not used, the alternate 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 $KMnO_4$ 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 (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 cloudly. 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 ($Na_2S_2O_3 \cdot 5H_2O$) or 15.8 g of anhydrous sodium thiosulfate ($Na_2S_2O_3$) in 1 liter of deionized, distilled water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) 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 (C_6H_5AsDO) 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.

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Note - A 0.01 N phenylarsine oxide solution may be prepared instead of 0.01 N thiosulfate (see Section 6.3.3).

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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 midget 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 to be conducted at the beginning and the end of the sample run. 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.

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.

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 to be conducted at the beginning and the end of the sample run. 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.

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.

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_2S 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 alternate 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.

7.2.3 (Alternate). 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_2S before adding any further rinses. Repeat the

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 alternate recovery procedure described below must be used.

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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_2S 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.

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 9.3. 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°C (360 to 390°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 to 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 9.1. 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°C (360 to 390°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 3 M 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

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 to 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 9.1. 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°C (360 to 390°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 3 M 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 9.2. 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 (as 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

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 (0.1 N) Thiosulfate Solution.

$$N_S = 2.039W/V_S$$

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_2/mole $K_2Cr_2O_7$) (1,000 ml/liter)/ = (294.2 g $K_2Cr_2O_7$/mole) (10 aliquot factor)

9.2 Normality of Standard Phenylarsine Oxide Solution (if applicable).

$$N_A = 0.2039\ W/V_A$$

where:

W = Weight of $K_2Cr_2O_7$ used, g.

V_A = Volume of $C_6H_5A_5O$ used, ml.

N_A = Normality of standard phenylarsine oxide solution, g=eg/liter.

0.2039 = Conversion factor

(6. eq. I_2/mole $K_2Cr_2O_7$) (1,000 ml/liter)/ = (249.2 g $K_2Cr_2O_7$/mole) (10 aliquot factor)

9.3 Normality of Standard Iodine Solution.

$$N_I = N_T V_T / V_I$$

where:

N_I = Normality of standard iodine solution, g-eg/liter.

V_I = Volume of standard iodine solution used, ml.

N_T = Normality of standard (0.01 N) thiosulfate solution; assumed to be 0.1 N_S. g-eq/liter.

V_T = Volume of thiosulfate solution used, ml.

N_S = Normality of standard thiosulfate solution, g-eq/liter.

2.039 = Conversion factor

(6. eq. I_2/mole $K_2Cr_2O_7$) (1,000 ml/liter)/ = (294.2 g $K_2Cr_2O_7$/mole) (10 aliquot factor)

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0.2039 = Conversion factor

(6. eq. I_2/mole $K_2Cr_2O_7$) (1,000 ml/liter)/ = (249.2 g $K_2Cr_2O_7$/mole) (10 aliquot factor)

9.3 Normality of Standard Iodine Solution.

$$N_I = N_T V_T/V_I$$

where:

N_I = Normality of standard iodine solution, g-eg/liter.

V_I = Volume of standard iodine solution used, ml.

N_T = Normality of standard (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 9.3 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°C) and 760 mm Hg.

$$V_{m(std)} = V_m Y \; [(T_{std}/T_m)(P_{bar}/P_{std})]$$

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°K.

T_m = Average dry gas meter temperature, °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_2S. Calculate the concentration of H_2S in the gas stream at standard conditions using the following equation:

$$C_{H_2S} = K[(V_{IT}N_I - V_{TT}N_T) \text{ sample} - (V_{IT}N_I - V_{TT}N_T) \text{ blank}]/V_{m(std)}$$

where (metric units):

C_{H_2S} = Concentraton of H_2S at standard conditions, mg/dscm.

K = Conversion factor = 17.04×10^3.

(34.07 g/mole H_2S) (1,000 liters/m^3) (1,000 mg/g)/ =
1,000 ml/liter) ($2H_2S$ 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 (~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 9.5 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.

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 (~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 9.5 with N_A and V_{AT}, respectively (see Sections 7.3.1 and 8.1.3).

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11. Bibliography

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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 usable 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 criteria set below 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 (H_2S), carbonyl sulfide (COS), and carbon disulfide (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 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 sample line, and by conditioning the smaple 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_2 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 eluding CO and CO_2, 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_2 in the

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 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

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3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 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 eluding CO and CO_2, 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_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of Section 4.1.

3.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling line can lead to eventual coating and even blockage of the sample line. This problem can be eliminated along with the moisture problem by heating the sample line.

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 8-hour period shall not exceed ±5 percent.

5. Apparatus

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allows calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 The sample line must be made of Teflon,[1/] no greater than 1.3 cm (1/2 in.) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120°C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120°C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert material (e.g., stainless steel or Teflon). It must be heated to 120°C and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. 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°C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1°C.

[1/] Mention of trade names or specific products does not constitute an endorsement by the Air Resources Board.

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5.3 Gas Chromatograph. 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°C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1°C.

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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.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H_2S, COS, and CS_2.

To demonstrate that adequate resolution has been achieved the tester must submit a chromatograph 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 fullscale. 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 Control Agency's Authorized Representative.

5.5.1 Calibration System. The calibration system must contain the following components.

5.5.2 Flow System. To measure air flow over permeation tubes at ±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 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1°C.

5.5.4 Temperature Gauge. Thermometer of equivalent to monitor bath temperature within ±1°C.

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5.5.4 Temperature Gauge. Thermometer of equivalent to monitor bath temperature within ±1°C.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) 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_2S, COS, and CS_2, 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.

7. Pretest Procedures

The following procedures are 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 the following procedures are to 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.

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 the of GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component

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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°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:

$$C = K \times Pr/ML$$

Equation 15-1

where

C = Concentration of permeant produced in ppm.

Pr = Permeation rate of the tube in ug/min.

M = Molecular weight of the permeant: g/g-mole.

L = Flow rate, l/min, of air over permeant @ 20°C, 760 mm Hg.

K = Gas constant at 20°C and 760 mm Hg = 24.04 l/g mole.

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°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:

$$C = K \times Pr/ML$$

Equation 15-1

where

C = Concentration of permeant produced in ppm.

Pr = Permeation rate of the tube in ug/min.

M = Molecular weight of the permeant: g/g-mole.

L = Flow rate, l/min, of air over permeant @ 20°C, 760 mm Hg.

K = Gas constant at 20°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 0.05 to 1.0 ppm) for each of the four 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.

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_2S (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 paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three more 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 paragraph 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.

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 paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three more 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.

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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. 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 sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

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 air may be used provided they are traceable to permeation tubes. 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 secton 8. Only H_2S (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 paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 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 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 air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

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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_2 Equivalent. SO_2 equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis.

$$SO_2 \text{ equivalent} = \sum (H_2S, COS, 2\ CS_2)d$$

Equation 15-2

where:

SO_2 equivalent = The sum of the concentration for each of the measured compounds (COS, H_2S, CS_2) expressed as sulfur dioxide in ppm.

H_2S = Hydrogen sulfide, ppm.

COS = Carbonyl sulfide, ppm.

CS_2 = Carbon disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average SO_2 equivalent will be determined as follows:

$$\text{Average } SO_2 \text{ equivalent} = \frac{\sum_{i=1}^{N} SO_2 \text{ equiv.}_i}{N\ (1 - Bwo)}$$

Equation 15-3

where:

Average SO_2 equivalent = Average SO_2 equivalent in ppm, dry basis.

SO_2 equivalent i = SO_2 in ppm as determined by Equation 15-2.

N = Number of analyses performed.

Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4 - Determination of Moisture in Stack Gases (36 FR 24887).

12 Example System

12.1 Apparatus

12.1.1 Sample System

12.1.1.1 Probe. Stainless steel tubing, 6.35 mm (1/4 in.) outside diameter, packed with glass wool.

12.1.1.2 Sample Line. 3/16 inch inside diameter Teflon tubing heated to 120°C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120°C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 15-2. The dilution system is constructed such that all sample contacts are

SO_2 equivalent i = SO_2 in ppm as determined by Equation 15-2.

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Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4 - Determination of Moisture in Stack Gases (36 FR 24887).

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12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120°C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 15-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120°C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1350 cc of clean dry air as shown in Figure 15-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120°C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min. ±1 percent per dilution stage.

12.1.3 Gas Chromatrograph.

12.1.3.1 Column - 1.83 m (6 ft.) length of Teflon tubing, 2.16 mm (0.085 in.) inside diameter, packed with deactivated silica gel, or equivalent.

12.1.3.2 Sample Valve. Teflon six port gas sampling valve, equipped with a 1 ml sample loop, actuated by compressed air (Figure 15-1).

12.1.3.3 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100°C, constant within ±1°C.

12.1.3.4 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1°C.

12.1.3.5 Flow System. Gas metering system to measure sample flow, hydrogen flow, oxygen flow and nitrogen carrier gas flow.

12.1.3.6 Detector. Flame photometric detector.

12.1.3.7 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

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12.1.3.7 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

12.1.3.8 Power Supply. Capable of delivering up to 750 volts.

12.1.3.9 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4 Calibration. Permeation tube system (Figure 15-3).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range of 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ± 2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30°C within ± 0.1°C.

12.2 Reagents.

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0°C.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30°C within ± 0.1°C.

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12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

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13. Bibliography

1. O'Keeffe, A.E. and G.C. Ortman. "Primary Standards for Trace Gas Analysis." Anal. Chem. 38,760 (1966).

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per Million Levels." Environmental Science and Technology 3:7 (July, 1969).

3. Mulick, J.D., R.K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6-8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." Pulp and Paper Magazine of Canada, 73,3 (March 1972).

5. Grimley, K.W., W.S. Smith, and R.M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, MO. June 14-19, 1970.

6. General Reference. Standard Methods of Chemical Analysis Volume III A and B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

12.3 Operating Parameters. The operating parameters for the GC/FPD system are as follows: nitrogen carrier gas flow rate of 100 cc/min., exhaust temperature of 110°C, detector temperature 105°C, oven temperature of 40°C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate of 80 cc/minute.

12.4 Analysis. The sample valve is actuated for 1 minute in which time an aliquot of dilute sample is injected onto the separation column. The valve is then deactivated for the remainder of analysis cycle in which time the sample loop is refilled and the separation column continues to be foreflushed. The elution time for each compound will be determined during calibration.

13. Bibliography

1. O'Keeffe, A.E. and G.C. Ortman. "Primary Standards for Trace Gas Analysis." Anal. Chem. 38,760 (1966).

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METHOD 16 - SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

INTRODUCTION

The method described below uses the principle of gas chromatographic separation and flame photometric detection. Since there are many systems or sets of operating conditions that represent usable 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 criteria set below 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 (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability: This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills.

2. Range and Sensitivity

2.1 Range. Coupled with a gas chromatographic system utilizing a ten milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 1 ppm. This limit is expanded by dilution of the sample gas before analysis. Kraft mill gas samples are normally diluted tenfold (9:1), resulting in an upper limit of about 10 ppm for each compound.

For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size to 1 milliliter.

2.2 Using the sample size, the minimum detectable concentration is approximately 50 ppb.

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 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_2 have substantial desensitizing effect on the flame photometric detector even after

2. Range and Sensitivity

2.1 Range. Coupled with a gas chromatographic system utilizing a ten milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 1 ppm. This limit is expanded by dilution of the sample gas before analysis. Kraft mill gas samples are normally diluted tenfold (9:1), resulting in an upper limit of about 10 ppm for each compound.

For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size to 1 milliliter.

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3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effect 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 these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of Section 4.1.

3.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference must be eliminated by use of a probe filter.

3.4 Sulfur Dioxide. SO_2 is not a specific interferent but may be present in such large amount that it cannot be effectively separated from other compounds of interest. The procedure must be designed to eliminate this problem either by the choice of separation columns or by removal of SO_2 from the sample. In the example system, SO_2 is removed by a citrate buffer solution prior to GC injection. This scrubber will be used when SO_2 levels are high enough to prevent baseline separation from the reduced sulfur compounds.

Compliance with this section can be demonstrated by submitting chromatographs of calibration gases with SO_2 present in the same quantities expected from the emission source to be tested.

Acceptable systems shall show baseline separation with the amplifier attenuation set so that the reduced sulfur compound of concern is at least 50 percent of full scale. Baseline separation is defined as a return to zero ± percent in the interval between peaks.

4. Precision and Accuracy

4.1 GC/FPD and Dilution System 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 ± 5 percent from the mean of the three injections.

4.2 GC/FPD and Dilution System Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8 hour period shall not exceed ± 5 percent.

4.3 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

5. Apparatus (See Figure 16-1).

5.1 Sampling.

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

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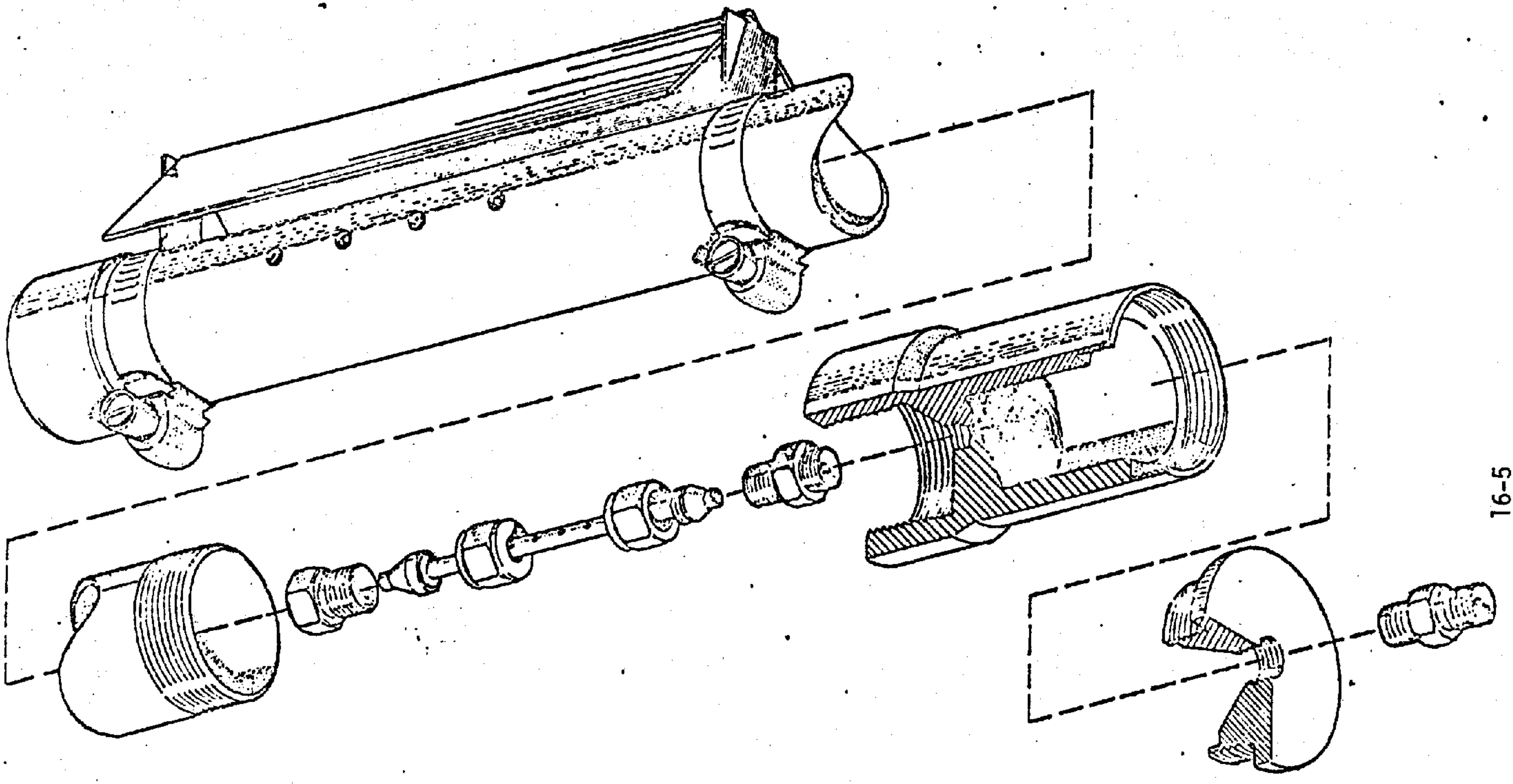

Figure 16-1. Probe used for sample gas containing high particulate loadings.

5.1.2 Sample Line. The sample line must be made of Teflon,[1] no greater than 1.3 cm (1/2 in.) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120°C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump heat must be heated to 120°C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert materials (e.g., stainless steel or Teflon). It must be heated to 120°C and be capable of approximately a 9:1 dilution of the sample.

5.3 SO_2 Scrubber. The SO_2 scrubber is a midget impinger packed with glass wool to eliminate entrained mist and charged with potassium citrate-citric acid buffer.

5.4 Gas Chromatograph. The gas chromatograph must have at least he following components:

5.4.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1°C.

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[1] Mention of trade names or specific products does not constitute endorsement by the Air Resources Board.

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5.4.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature $\underline{+}1^{o}C$.

5.4.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.4.4 Flame Photometric Detector.

5.4.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.4.4.2 Power Supply. Capable of delivering up to 750 volts.

5.4.4.3 Recorder. Compatible with the output voltage range of the electrometer.

5.5 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatograph of a calibration gas containing all four of the TRS 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 in Section 3.4. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Control Agency's Authorized Representative.

5.6 Calibration System. The calibration system must contain the following components:

5.6.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.6.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flow meter 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 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lower flow measurement. Calibration with a wet test meter before a test is optional.

5.6.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1°C.

5.6.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1°C.

set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined in Section 3.4. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Control Agency's Authorized Representative.

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5.6.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flow meter 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 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lower flow measurement. Calibration with a wet test meter before a test is optional.

5.6.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1°C.

5.6.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1°C.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons. This gas must be heated prior to mixing with the sample to avoid water condensation at the point of contact.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, 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 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. Two hundred eighty-four grams of sodium citrate may be substituted for the potassium citrate.

7. Pretest Procedures.

The following procedures are 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 are to 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.

6.6 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. Two hundred eighty-four grams of sodium citrate may be substituted for the potassium citrate.

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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. In any component, or if 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.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibraton temperature of the tubes within $\pm 0.1^{\circ}C$. 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:

$$C = K\left(\frac{P_r}{ML}\right)$$

Equation 16-1

where:

C = Concentration of permeant produces in ppm.

P_r = Permeation rate of the tube in ug/min.

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Equation 16-1

where:

C = Concentration of permeant produces in ppm.

P_r = Permeation rate of the tube in ug/min.

M = Molecular weight of the permeant (g/g-mole).
L = Flow rate, l/min, of air over permeant @ 20°C, 760 mm Hg.
K = Gas constant at 20°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 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, but using the SO_2 scrubber, 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 processing.

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.

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_2S (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 paragraph. 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 paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

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9.2 Analysis. Aliquots of diluted sample pass through the SO_2 scrubber, and then 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. 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 sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

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 insure 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.

For sampling losses greater than 20 percent in a sample run, the sample run is not to be used when determining the arithmetic mean of the performance test. For sampling losses of 0-20 percent, the sample concentration must be corrected by dividing the sample concentration by the fraction of recovery. The fraction of recovery is equal to one minus the ratio of the measured concentration to the known concentration of hydrogen sulfide in the sample line loss procedure. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. 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_2S (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 paragraph 10.1. The calibration drift should not exceed the limits set forth in subsection 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.

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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 square line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$\text{TRS} = \sum(\text{H}_2\text{S, MeSH, DMS, 2 DMDS})d$$

Equation 16-2

where:

TRS = Total reduced sulfur in ppm, wet basis.

H_2S = Hydrogen sulfide, ppm.

MeSH = Methyl mercaptan, ppm.

DMS = Dimethyl sulfide, ppm.

DMDS = Dimethyl disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \frac{\sum_{i=1}^{N} \text{TRS}_i}{N(1-B_{wo})}$$

where:

Average TRS = Average total reduced sulfur in ppm, dry basis.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16-2.

N = Number of samples

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Reference Method 1-4 - Determination of Moisture in Stack Gases.

11.4 Average concentration of individual reduced sulfur compounds.

$$C = \frac{\sum_{i=1}^{N} s_i}{N}$$

Equation 16-3

where:

s_i = Concentration of any reduced sulfur compound in the ith sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12. Example System

12.1 Apparatus

12.1.1 Sampling System

12.1.1.1 Probe. Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes and the glass wool plugs to reduce clogging of the filter and possible

N = Number of samples

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12.1.1.2 Sample Line 3/16 inch inside diameter Teflon tubing, heated to 120°C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120°C by enclosing it in the sample dilution box (12.1.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 16-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120°C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1,350 cc of clean dry air as shown in Figure 16-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120°C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flow meters. Rotameters or equivalent to measure flow from 0 to 1,500 ml/min ±1 percent per dilution stage.

12.1.3 SO_2 Scrubber. Midget impinger with 15 ml of potassium citrate buffer to absorb SO_2 in the sample.

12.1.4 Gas Chromatograph Columns. Two types of columns are used for separation of low and high molecular weight sulfur compounds:

accomplished by combining 150 cc of sample with 1,350 cc of clean dry air as shown in Figure 16-2.

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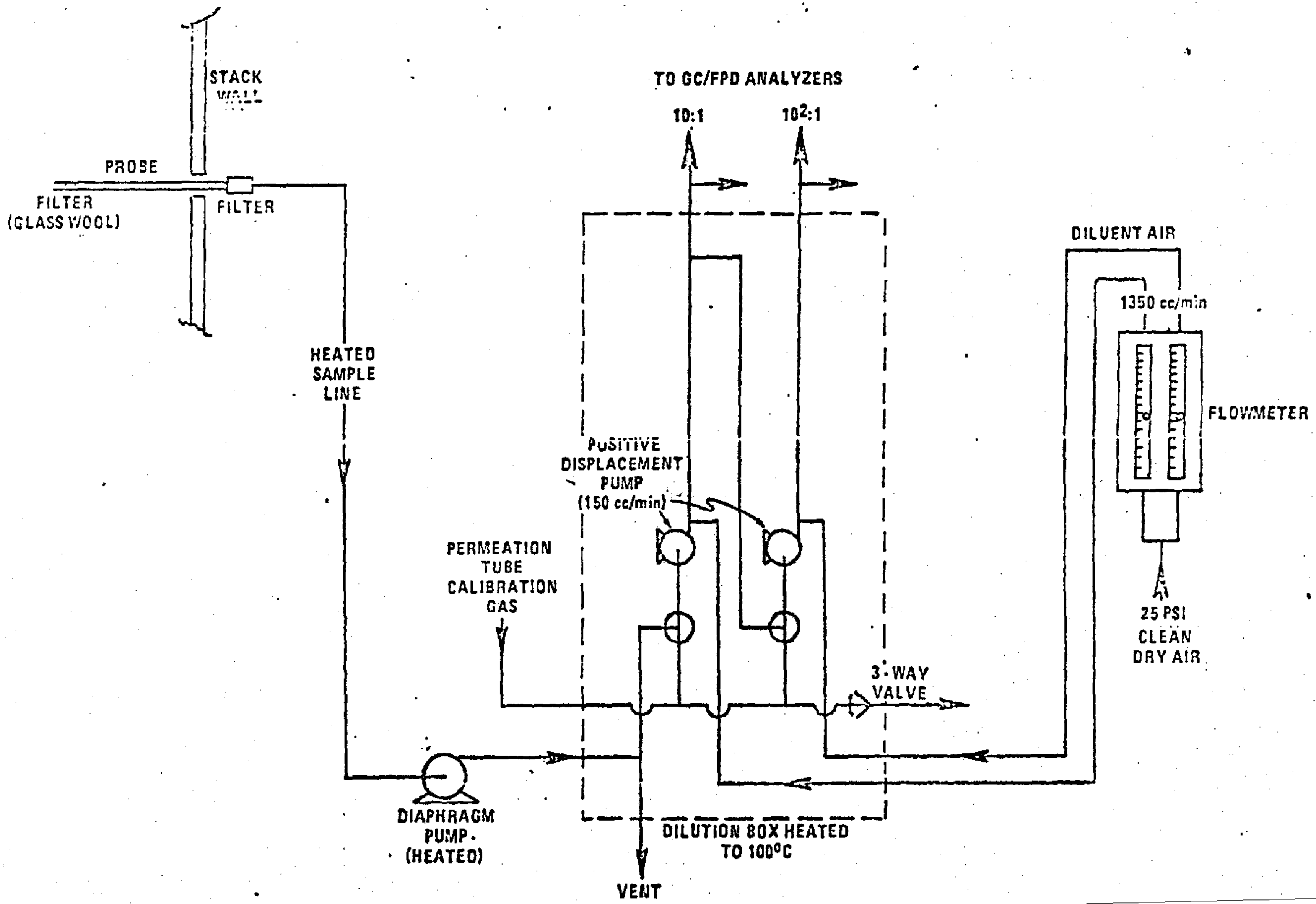

Figure 16-2. Sampling and dilution apparatus.

12.1.4.1 Low Molecular Weight Sulfur Compounds Column (GC/FPD-I).

12.1.4.1.1 Separation Column. 11 m by 2.16 mm (36 ft. by 0.085 in.) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 5 percent polyphenyl ether and 0.05 percent orthophosphoric acid, or equivalent (see Figure 16-3).

12.1.4.1.2 Stripper or Precolumn. 0.6 m by 2.16 mm (2 ft. by 0.085 in.) inside diameter Teflon tubing.

12.1.4.1.3 Sample Valve. Teflon 10-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.4.1.4 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100°C, constant within ±1°C.

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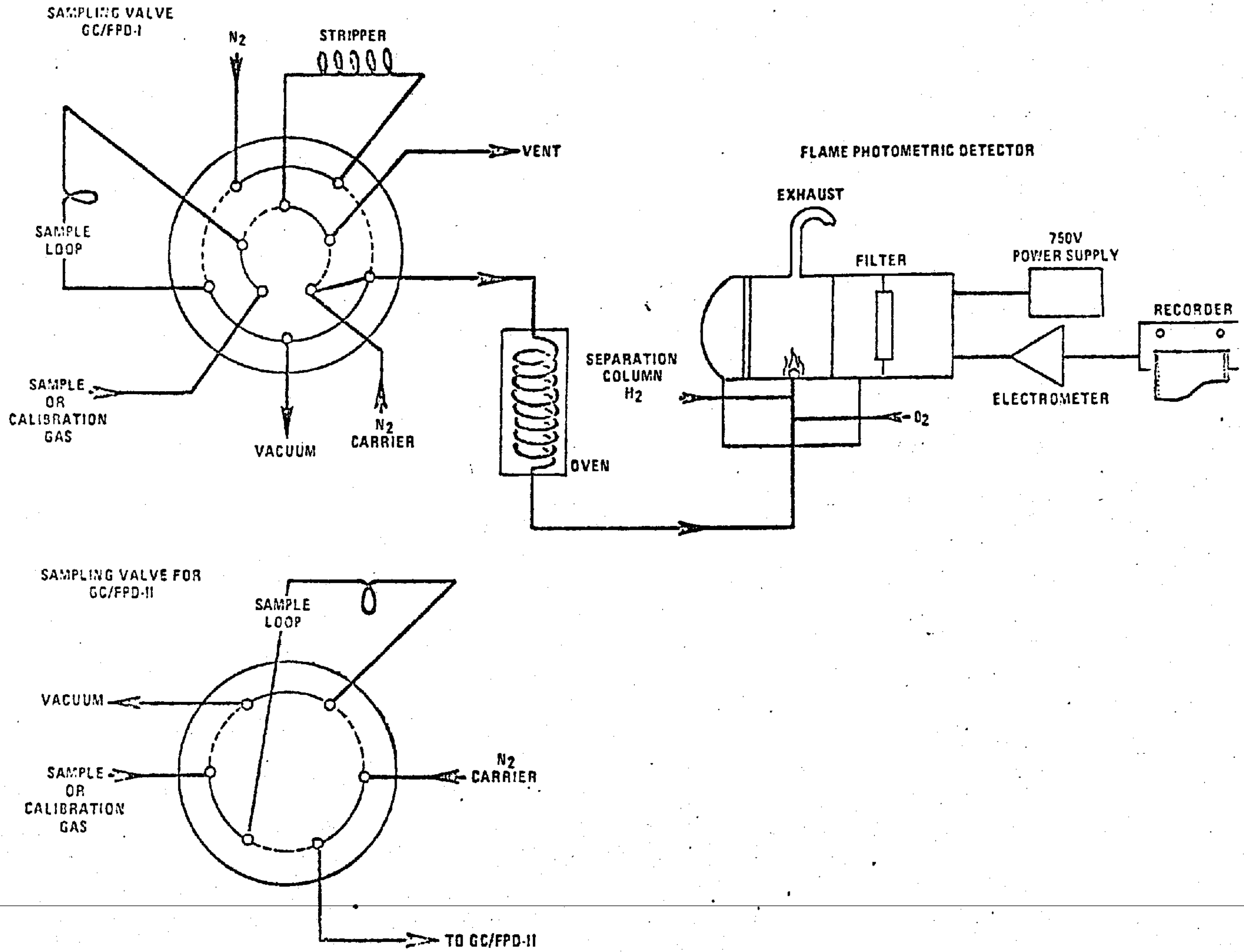

Figure 16-3. Gas chromatographic-flame photometric analyzers.

12.1.4.1.5 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1°C.

12.1.4.1.6 Flow System. Gas metering system to measure sample flow, hydrogen flow, and oxygen flow (and nitrogen carrier gas flow).

12.1.4.1.7 Detector. Flame photometric detector.

12.1.4.1.8 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

12.1.4.1.9 Power Supply. Capable of delivering up to 750 volts.

12.1.4.1.10 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4.2 High Molecular Weight Compounds Column (GC/FPD-II).

12.1.4.1.5 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1°C.

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12.1.4.1.9 Power Supply. Capable of delivering up to 750 volts.

12.1.4.1.10 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4.2 High Molecular Weight Compounds Column (GC/FPD-II).

12.1.4.2.1 Separation Column. 3.05 m by 2.16 mm (10 ft by 0.085 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton X-305, or equivalent.

12.1.4.2.2 Sample Valve. Teflon 6-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.4.2.3 Other Components. All components same as in 12.1.4.1.4 to 12.1.4.1.10.

12.1.5 Calibration. Permeation tube system (Figure 16-4).

12.1.5.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.5.2 Mass Flow meters. Two mass flow meters in the range 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ±2 percent. These flow meters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flow meters,

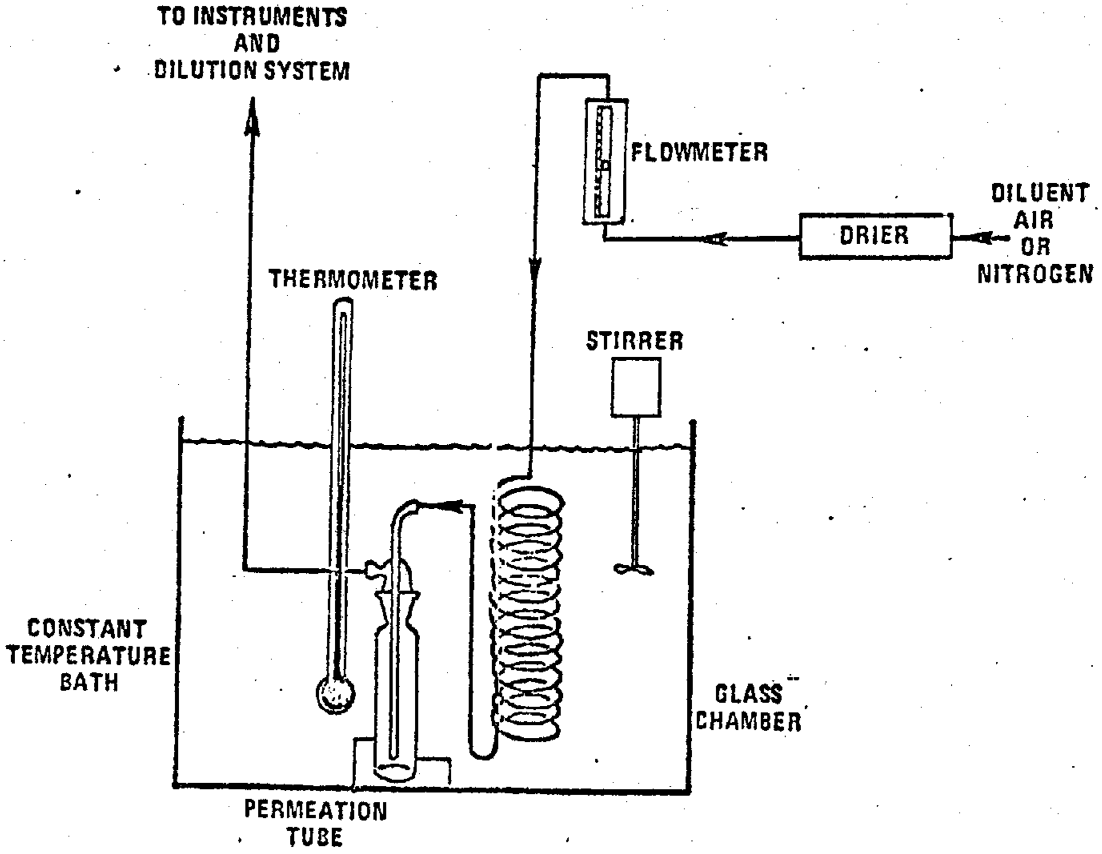

Figure 16-4. Apparatus for field calibration.

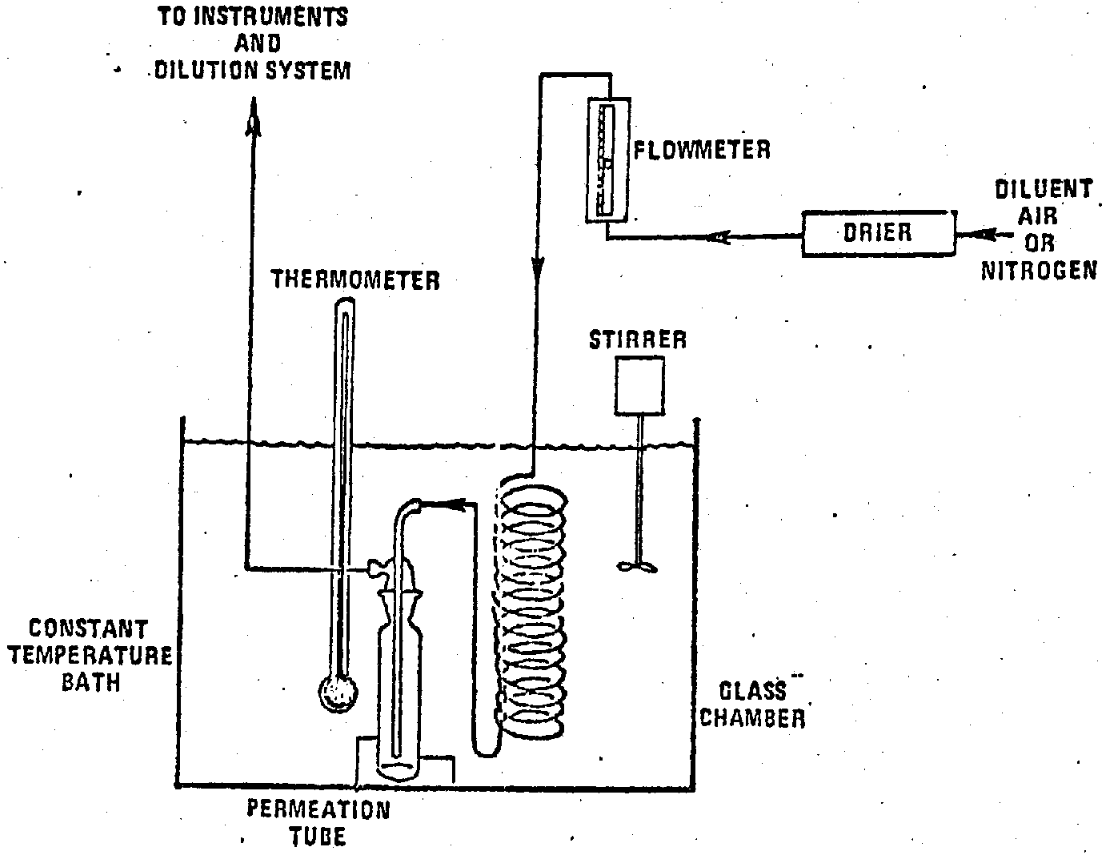

Figure 16-4. Apparatus for field calibration.

set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flow meter followed by injection of calibration gas at the same flow rate as measured by the other flow meter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flow meter shall be calibrated prior to the first test with a wet test meter and thereafter, at least once each year.

12.1.5.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30°C, within ±0.1°C.

12.2 Reagents

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in Section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibrated Gases. Permeation tubes gravimetrically calibrated and certified at 30.0°C.

12.2.7 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. 284 grams of sodium citrate may be substituted for the potassium citrate.

12.3 Operating Parameters

12.3.1 Low-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/min., exhaust temperature of 110°C, detector temperature of 105°C, oven temperature of 40°C, hydrogen flow rate of 80 cc/min., oxygen flow rate of 20 cc/min., and sample flow rate between 20 and 80 cc/min.

12.2.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in Section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibrated Gases. Permeation tubes gravimetrically calibrated and certified at 30.0^{o}C.

12.2.7 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. 284 grams of sodium citrate may be substituted for the potassium citrate.

12.3 Operating Parameters

12.3.1 Low-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/min., exhaust temperature of 110^{o}C, detector temperature of 105^{o}C, oven temperature of 40^{o}C, hydrogen flow rate of 80 cc/min., oxygen flow rate of 20 cc/min., and sample flow rate between 20 and 80 cc/min.

12.3.2 High-Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system for high molecular weight compounds are the same as in 12.3.1 except: oven temperature of 70°C, and nitrogen carrier gas flow of 100 cc/min.

12.4 Analysis Procedure.

12.4.1 Analysis. Aliquots of diluted sample are injected simultaneously into both GC/FPD analyzers for analysis. GC/FPD-I is used to measure the low-molecular weight reduced sulfur compounds. The low-molecular weight compounds include hydrogen sulfide, methyl mercaptan, and dimethyl sulfide. GC/FPD-II is used to resolve the high-molecular weight compound. The high-molecular weight compound is dimethyl disulfide.

12.4.1.1 Analysis of Low-Molecular Weight Sulfur Compounds. The sample valve is actuated for 3 minutes in which time an aliquot of diluted sample is injected into the stripper column and analytical column. The valve is then deactivated for approximately 12 minutes in which time, the analytical column continues to be foreflushed, the stripper column is backflushed, and the sample loop is refilled. Monitor the responses. The elution time for each compound will be determined during calibration.

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METHOD 17 - DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES (IN-STACK FILTRATION METHOD)

INTRODUCTION

Particulate matter is not an absolute quantity; rather, it is a function of temperature and pressure. Therefore, to prevent variability in particulate matter emission regulations and/or associated test methods, the temperature and pressure at which particulate matter is to be measured must be carefully defined. Of the two variables (i.e., temperature and pressure), temperature has the greater effect upon the amount of particulate matter in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible.

In Method 5, 250°F is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standards, particulate matter is defined with respect to temperature. In order to maintain a collection temperature of 250°F, Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where particulate matter concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and heating system, and sample at stack temperature.

This method describes an in-stack sampling system and sampling procedures for use in such cases. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Control Agency's Authorized Representative.

1. Principle and Applicability

1.1 Principle: Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The particulate mass is determined gravimetrically after removal of uncombined water.

1.2 Applicability: This method applies to the determination of particulate emissions from stationary sources for determining compliance with new source performance standards, only when specifically provided for in an applicable subpart of the standards. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see Section 4.1.2).

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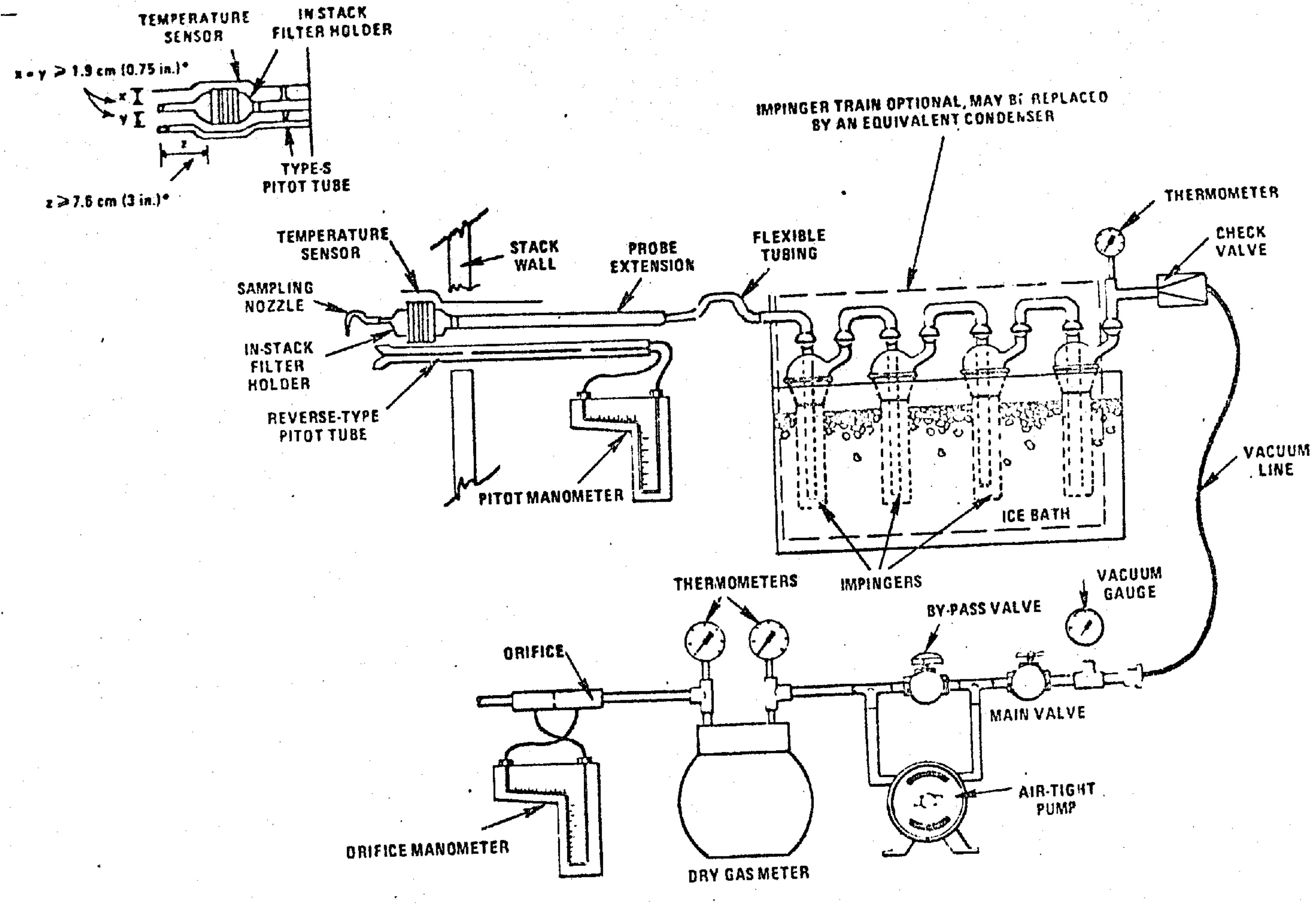
2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17-1. Construction details for many, but not all, of the train components are given in APTD-0581 (Citation 2 in Section 7); for changes from the APTD-0581 document and for allowable modifications to Figure 17-1, consult with the Executive Officer. The operating and maintenance procedures for many of the sampling train components are described in APTD-0576 (Citation 3 in Section 7). 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. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass, with sharp, tapered leading edge. The angle of taper shall be 30^o 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 Control Agency's Authorized Representative. 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 Control Agency's Authorized Representative.



*SUGGESTED (INTERFERENCE-FREE) SPACINGS

Figure 17-1. Particulate-Sampling Train, Equipped with In-Stack Filter.

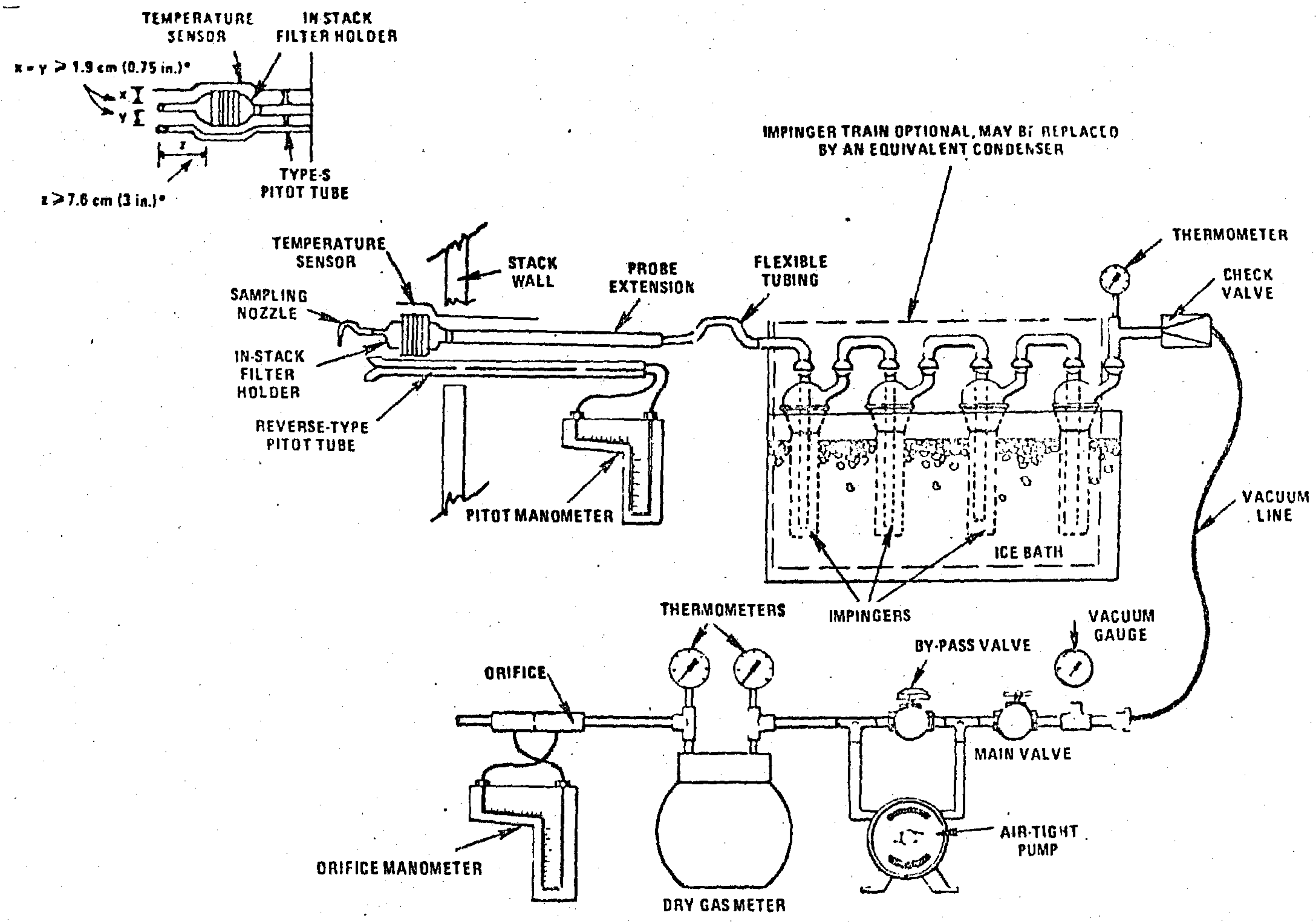


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Figure 17-1. Particulate-Sampling Train, Equipped with In-Stack Filter.

A range of sizes suitable for isokinetic sampling should be available, e.q. 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 outlines in Section 5.1.

2.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass, or stainless steel; if a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used subject to the approval of the Control Agency's Authorized Representative. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

2.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

2.1.4 Pitot Tube. Type S, as described in Section 2.1 of Method 2 or other device approved by the Control Agency's Authorized Representative , the pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity (see Figure 17-1). The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane during sampling (see Method 2, Figure 2-6b). It is recommended: (1) that the pitot tube have a known baseline coefficient, determined as outlined in Section 4 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17-1). Note that the 1.9 cm (0.75 in) free-space between the nozzle and pitot tube shown in Figure 17-1, is based on a 1.3 cm (0.5 in) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free space shall be 1.9 cm (0.75 in.) with the largest sized nozzle in place.

Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17-1 (or the equivalent of these requirements, e.g., Figure 2-7 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Control Agency's Authorized Representative.

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2.1.5 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 (ΔP) readings, and the other, for orifice differential pressure readings.

2.1.6 Condenser. It is recommended that the impinger system described in Method 5 be used to determine the moisture content of the stack gas. Alternatively, any system that allows measurement of both the water condensed and the moisture leaving the condenser, each to within 1 ml or 1 g, may be used. The moisture leaving the condenser can be measured either 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 silica gel trap with exit gases kept below $20^{o}C$ ($68^{o}F$) and determining the weight gain.

Flexibile tubing may be used between the probe extension and condenser. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel 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.

2.1.7 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 17-1. 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 Control Agency's Authorized Representative. 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 described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.8 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

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2.1.8 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.

2.1.9 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 be attached to either the pitot tube or to the probe extension, in a fixed configuration. If the temperature sensor is attached in the field; the sensor shall be placed in an interference-free arrangement with respect to the Type S pitot tube openings (as shown in Figure 17-1 or in Figure 2-7 of Method 2). Alternatively, the temperature sensor need not be attached to either the probe extension of pitot tube during samplng, provided that a difference of not more than 1 percent in the average velocity measurement is introduced. This alternative is subject to the approval of the Control Agency's Authorized Representative.

2.2 Sample Recovery.

2.2.1 Probe Nozzle Brush. Nylon bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe 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 botles for longer than a month.

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

2.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Control Agency's Authorized Representative.

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.

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

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

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

2.3 Analysis.

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 mg.

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.

3.1.1 Filters. The in-stack filters shall be glass mats or thimble fiber filters, without organic binders, and shall exhibit at least 99.5 percent efficiency (00.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175^{O}C (350^{O}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 Control Agency's Authorized Representative.

3.1.3 Crushed Ice.

3.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. Ths 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 Control Agency's Authorized Representative.

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3.2 Sample Recovery. Acetone, reagent grade, 0.001 percent residue, in glass bottles. 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 (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.

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 Control Agency's Authorized Representative.

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. All components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

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 its 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 size on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6°C (68±10°F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Control Agency's Authorized Representative), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, 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 its impinger or sampling holder just prior to train assembly.

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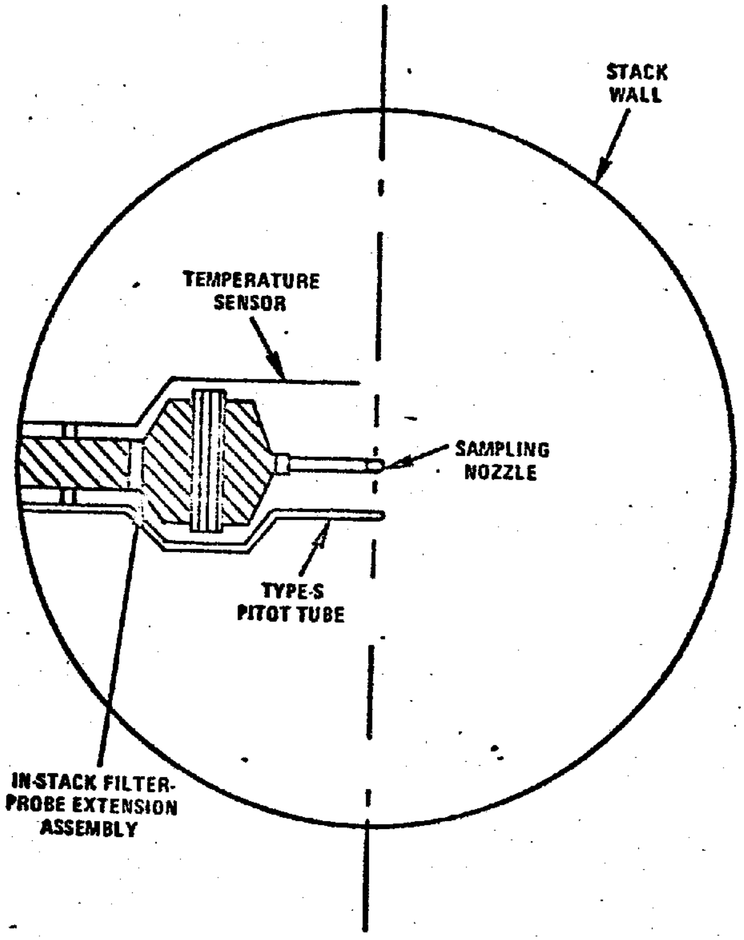
4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Control Agency's Authorized Representative. Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17-2. Calculate the estimated cross-section blockage, as shown in Figure 17-2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Control Agency's Authorized Representative. (See Citation 10 in Section 7.) 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



$$\text{ESTIMATED BLOCKAGE (\%)} = \left[\frac{\text{SHADED AREA}}{\text{DUCT AREA}}\right] \times 100$$

Figure 17-2. Projected-area model of cross-section blockage (approximate average for a sample traverse) caused by an in-stack filter holder-probe extension assembly.

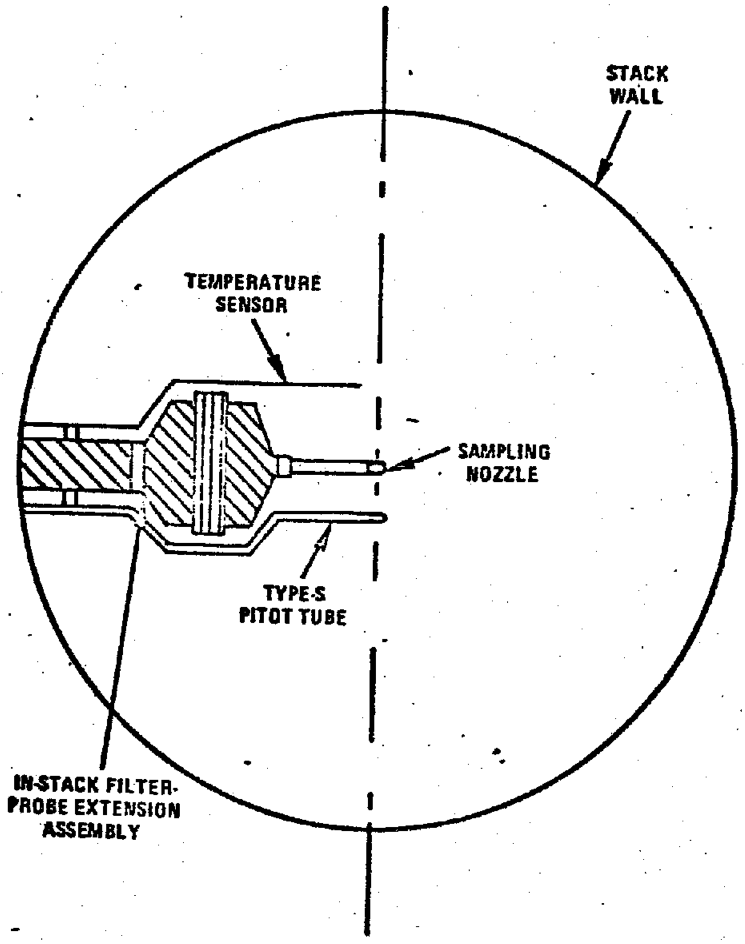


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Figure 17-2. Projected-area model of cross-section blockage (approximate average for a sample traverse) caused by an in-stack filter holder-probe extension assembly.

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 particular 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 probe extension 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 minutes (or some greater than interval if specified by the Control Agency's Authorized Representative), 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.

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 Control Agency's Authorized Representative '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.

If impingers are used to condense stack gas moisture, prepare them as follows: place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximtely 200 to 300 g of preweighed some greater than interval if specified by the Control Agency's Authorized Representative), 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.

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If impingers are used to condense stack gas moisture, prepare them as follows: place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximtely 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.

If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

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 not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 17-1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

4.1.4 Leak Check Procedures

4.1.4.1 Pretest Leak-Check. A pretest leak-check is required. The following procedure shall be used.

After the sampling train has been assembled, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg); note that a lower vacuum may be used, provided that it is not exceeded during the test. Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve contamination by the silicone grease. Place crushed ice around the impingers.

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After the sampling train has been assembled, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg); note that a lower vacuum may be used, provided that it is not exceeded during the test. Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse direction of by-pass valve. 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 nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

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^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are to be done per the procedure outlined in Section 4.1.4.1 above.

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^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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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^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain a sampling rate such that sampling is within 10 percent of true isokinetic, unless otherwise specified by the Control Agency's Authorized Representative.

For each run, record the data required on the example data sheet shown in Figure 17-3. 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 required by Figure 17-3 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 the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the

PLANT ____________
LOCATION ____________
OPERATOR ____________
DATE ____________
RUN NO. ____________
SAMPLE BOX NO. ____________
METER BOX NO. ____________
METER $\Delta H_@$ ____________
C FACTOR ____________
PITOT TUBE COEFFICIENT, Cp ____________

SCHEMATIC OF STACK CROSS SECTION

BAROMETRIC PRESSURE ____________
ASSUMED MOISTURE, % ____________
PROBE EXTENSION LENGTH, m(ft.) ____________
NOZZLE IDENTIFICATION NO. ____________
AVERAGE CALIBRATED NOZZLE DIAMETER cm (in.) ____________
FILTER NO. ____________
LEAK RATE, m^3/min, (cfm) ____________
STATIC PRESSURE, mm Hg (in. Hg) ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S), °C (°F)	VELOCITY HEAD (ΔP_S), mm H_2O (in. H_2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H_2O (in. H_2O)	GAS SAMPLE VOLUME, m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET, °C (°F)	OUTLET, °C (°F)	
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 17-3. Particulate field data.

PLANT ____________
LOCATION ____________
OPERATOR ____________
DATE ____________
RUN NO. ____________
SAMPLE BOX NO. ____________
METER BOX NO. ____________
METER $\Delta H_@$ ____________
C FACTOR ____________
PITOT TUBE COEFFICIENT, Cp ____________

SCHEMATIC OF STACK CROSS SECTION

BAROMETRIC PRESSURE ____________
ASSUMED MOISTURE, % ____________
PROBE EXTENSION LENGTH, m(ft.) ____________
NOZZLE IDENTIFICATION NO. ____________
AVERAGE CALIBRATED NOZZLE DIAMETER cm (in.) ____________
FILTER NO. ____________
LEAK RATE, m^3/min, (cfm) ____________
STATIC PRESSURE, mm Hg (in. Hg) ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S), °C (°F)	VELOCITY HEAD (ΔP_S), mm H_2O (in. H_2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H_2O (in. H_2O)	GAS SAMPLE VOLUME, m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET, °C (°F)	OUTLET, °C (°F)	
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 17-3. Particulate field data.

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 to 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 Section 7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. 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 Control Agency's Authorized Representative , being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain a temperature of less than 20^{0}C (68^{0}F) at the condenser outlet; this will prevent excessive moisture losses. 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 holder assembly be used rather than attempting to change the filter itself. Before a new filter holder is installed, conduct a leak check, as outlined in Section 4.1.4.2. The total particulate weight shall include the summation of all filter assembly catches.

Traverse the stack cross section, as required by Method 1 or as specified by the Control Agency's Authorized Representative , being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

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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 holder assembly be used rather than attempting to change the filter itself. Before a new filter holder is installed, conduct a leak check, as outlined in 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 Control Agency's Authorized Representative. Not that when two or more trains are used, a separate analysis of the collected particulate from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the particulate catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Section 3.1 of Method 2; 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 Section 6.11) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Control Agency's Authorized Representative for possible variance on the isokinetic rates.

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

When the assembly 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, forcing condenser water backward.

Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension maintaining isokinetic rates due to source conditions, consult with the Control Agency's Authorized Representative for possible variance on the isokinetic rates.

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

When the assembly 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, forcing condenser water backward.

Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

Transfer both the filter holder-probe nozzle assembly and the condenser 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 nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these compounds with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Control Agency's Authorized Representative and shall be used when specified by the Control Agency's Authorized Representative , in these cases, save a water blank and follow Control Agency's Authorized Representative'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 acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

Container No. 2. Taking care to see that dust on the outside of the probe nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these compounds with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Control Agency's Authorized Representative and shall be used when specified by the Control Agency's Authorized Representative , in these cases, save a water blank and follow Control Agency's Authorized Representative'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 acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease (if applicable), 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 final rinse of the brush and filter holder. After all acetone washings and particulate matter are 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. If silica gel is used in the condenser system for moisture content determination, note the color of the gel to determine if it has been completely spent; make a notation of its condition. Transfer the silica gel back to its original container and seal. A funnel may make it easier to pour the silica gel without spilling, and a rubber policeman may be used as an aid in removing the silica gel. It is not necessary to remove the small amount of dust 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, follow the procedure for Container No. 3 under "Analysis."

Condenser Water. Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the liquid volume to within ±1 ml by using a graduated cylinder or, if a balance is available, determine the liquid weight to within ±0.5 g. Record the total 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.

4.3 Analysis. Record the data required on the example sheet shown in Figure 17-4. Handle each sample container as follows:

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 the average stack temperature or 105°C (220°F), whichever is less, for 2 to 3

Condenser Water. Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the liquid volume to within ±1 ml by using a graduated cylinder or, if a balance is available, determine the liquid weight to within ±0.5 g. Record the total 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.

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Alternatively, the sample may be oven dried at the average stack temperature or 105°C (220°F), whichever is less, for 2 to 3

105°C (220°F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Plant ______________________________

Date ______________________________

Run No. ______________________________

Filter No. ______________________________

Amount liquid lost during transport ______________________________

Acetone blank volume, ml ______________________________

Acetone wash volume, ml ______________________________

Acetone black concentration, mg/mg (equation 17-4) ______________________________

Acetone wash blank, mg (equation 17-5) ______________________________

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 (1g/ml).

$$\frac{\text{INCREASE, g}}{1\ \text{g/ml}} = \text{VOLUME WATER, ml}$$

Figure 17-4. Analytical data.

hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Control Agency's Authorized Representative. The tester may also opt to oven dry the sample at the average stack temperature or 105°C (220°F), whichever is less, 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 Control Agency's Authorized Representative , 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. 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.

"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 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Control Agency's Authorized Representative. The tester may also opt to oven dry the sample at the average stack temperature or 105°C (220°F), whichever is less, 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 Control Agency's Authorized Representative , 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.

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"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.

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. If the pitot tube is placed in an interference-free arrangement with respect to the other probe assembly components, its baseline (isolated tube) coefficient shall be determined as outlined in Section 4 of Method 2. If the probe assembly is not interference-free, the pitot tube assembly coefficient shall be determined by calibration, using methods subject to the approval of the Control Agency's Authorized Representative.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values.

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 0.00057 m^3/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^3/min (0.02 cfm).

5.2 Pitot Tube. If the pitot tube is placed in an interference-free arrangement with respect to the other probe assembly components, its baseline (isolated tube) coefficient shall be determined as outlined in Section 4 of Method 2. If the probe assembly is not interference-free, the pitot tube assembly coefficient shall be determined by calibration, using methods subject to the approval of the Control Agency's Authorized Representative.

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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 calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Control Agency's Authorized Representative.

NOTE: 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 which ever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 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.

5.5 Leak Check of Metering System Shown in Figure 17-1. 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 17-5). 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.

5.6 Barometer. Calibrate against a mercury barometer.

6. Calculations

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

6.1 Nomenclature.

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

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

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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.

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

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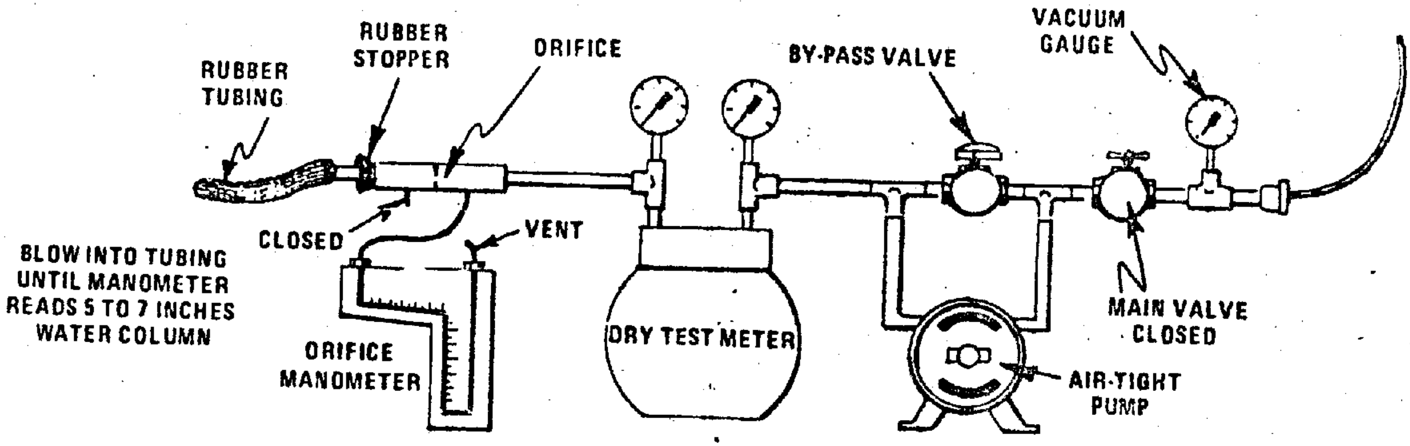

Figure 17-5. Leak check of meter box.

C_a = Acetone blank residue concentration, mg/g.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/sdcf).

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^3/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 "ith" component change (i = 1, 2, 3, ...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

m_n = Total amount of particulate matter collected, mg.

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

m_a = Mass of residue of acetone after evaporation, mg.

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

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

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

R = Ideal gas constant, 0.06236 mm Hg-m^3/^{o}K-g-mole (21.85 in Hg-ft^3/^{o}R-lb-mole).

C_a = Acetone blank residue concentration, mg/g.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/sdcf).

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^3/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 "ith" component change (i = 1, 2, 3, ...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

m_n = Total amount of particulate matter collected, mg.

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

m_a = Mass of residue of acetone after evaporation, mg.

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

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

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

R = Ideal gas constant, 0.06236 mm Hg-m^3/^oK-g-mole (21.85 in Hg-ft^3/^oR-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 17-3, °K (°R).

T_s = Absolute average stack gas temperature (see Figure 17-3, °K (°R).

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

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 17-4), ml.

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

$V_{m(std)}$ = Volume of gas sample as measured by dry gas meter, corrected to standard conditions, dcm (dcf).

$V_{w(std)}$ = 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 17, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration coefficient.

ΔH = Average pressure differential across the orifice meter (see Figure 17-3), mm H_2O (in H_2O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min.

θ_i = Sampling time interval, from the beginning of a run until the first component change, min.

θ_1 = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (nth) 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 17-3).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20^{0}C, 760 mm Hg or 68^{0}F, 29.92 in Hg) by using Equation 17-1.

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

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

Equation 17-1

where:

K_1 = 0.3858^{0} K/mm Hg for metric units; 17.65^{0} R/in Hg for English units.

θ_i = Sampling time interval, from the beginning of a run until the first component change, min.

θ_1 = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

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

Equation 17-1

where:

K_1 = 0.3858° K/mm Hg for metric units; 17.65° R/in Hg for English units.

NOTE: Equation 17-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 17-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 17-1 with the expressions:

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

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 17-1 by the expression:

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

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

6.4 Volume of Water Vapor.

$$V_{w(std)} = V_{1c} \left[\frac{P_w}{M_w}\right]\left[\frac{RT_{std}}{P_{std}}\right] = K_2 V_{1c}$$

Equation 17-2

where:

K_2 = 0.001333 m^3/ml for metric units; 0.04707 ft^3/ml for English units.

6.5 Moisture Content.

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

Equation 17-3

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \quad p_a}$$

Equation 17-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_a w p_a$$

Equation 17-5

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 17-4).

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.

$$c_s = (0.001 \text{ g/mg}) \ (m_n / V_{m(std)})$$

Equation 17-6

6.10 Conversion Factors:

From	To	Multiply by
scf.	m^3.	0.02832
g/ft^3.	gr/ft^3	15.43
g/ft^3.	lb/ft^3	2.205×10^{-3}
g/ft^3.	g/m^3	35.31

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a \quad p_a}$$

Equation 17-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} p_a$$

Equation 17-5

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 17-4).

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.

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g/ft^3.	gr/ft^3	15.43
g/ft^3.	lb/ft^3	2.205×10^{-3}
g/ft^3.	g/m^3	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation from Raw Data.

$$I = \frac{100\ T_s\ [K_3 V_{1c} + (V_m Y/T_m)(P_{bar} + \Delta H/13.6)]}{60\ \theta v_s\ P_s\ A_n}$$

Equation 17-7

where:

K_3 = 0.003454 mm Hg-m^3/ml-°K for metric units;

0.002669 in.Hg-ft^3/ml-°R for English units.

6.11.2 Calculation from Intermediate Values.

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

$$= K_4 \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})}$$

Equation 17-8

where:

K_4 = 4.320 for metric units; 0.09450 for English units.

6.12 Acceptable Results. If 90 percent $\leq I \leq$ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Control Agency's Authorized Representative may opt to accept the results. Otherwise, reject the results and repeat the test.

7. Bibliography

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. December 6, 1967.

2. Martin, Robert M., Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0581. April 1971.

3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March, 1972.

4. Smith, W.S., R.T. Shigehara, and W.F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, MO. June 14-19, 1970.

5. Smith, W.S., et al., Stack Gas Sampling Improved and Simplified with New Equipment. APCA Paper No. 67-119. 1967.

6. Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. 1967.

7. Shigehara, R.T. Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News 2:4-11. October, 1974.

8. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November, 1976 (unpublished paper).

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 617-622.

10. Vollaro, R.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. November, 1976.

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8. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November, 1976 (unpublished paper).

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 617-622.

10. Vollaro, R.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. November, 1976.

METHOD 100 - PROCEDURES FOR CONTINUOUS GASEOUS EMISSION STACK SAMPLING

1. Principle and Applicability

1.1 Principle: A sample of an exhaust gas stream is extracted, conditioned and analyzed continuously by instruments. The measurements made by the continuous analyzers are used to determine average emission concentrations. By measuring the stack gas flowrate and using this information with the average emission concentration mass emission rates can be determined:

1.2 Applicability: This method is applicable for determining emissions of Oxides of Nitrogen, Carbon Monoxide, Carbon Dioxide, Sulfur Dioxide, Total Hydrocarbons, and Oxygen from stationary source flowing gas streams in ducts, stacks and flues except for turbine engines and stationary diesel engines. This procedure does not supercede the New Source Performance Standards requirement for permanently installed continuous monitoring instruments.

This test procedure is an alternative method to appropriate U.S. EPA reference methods, in particular EPA methods 3, 6, 7 and 10. This procedure should be used only on those sources where equivalency to the reference methods has been established or the specific regulations for the source specify this procedure.

FIGURE 1-1

Example - PITOT TUBE - SAMPLE PROBE ASSEMBLY

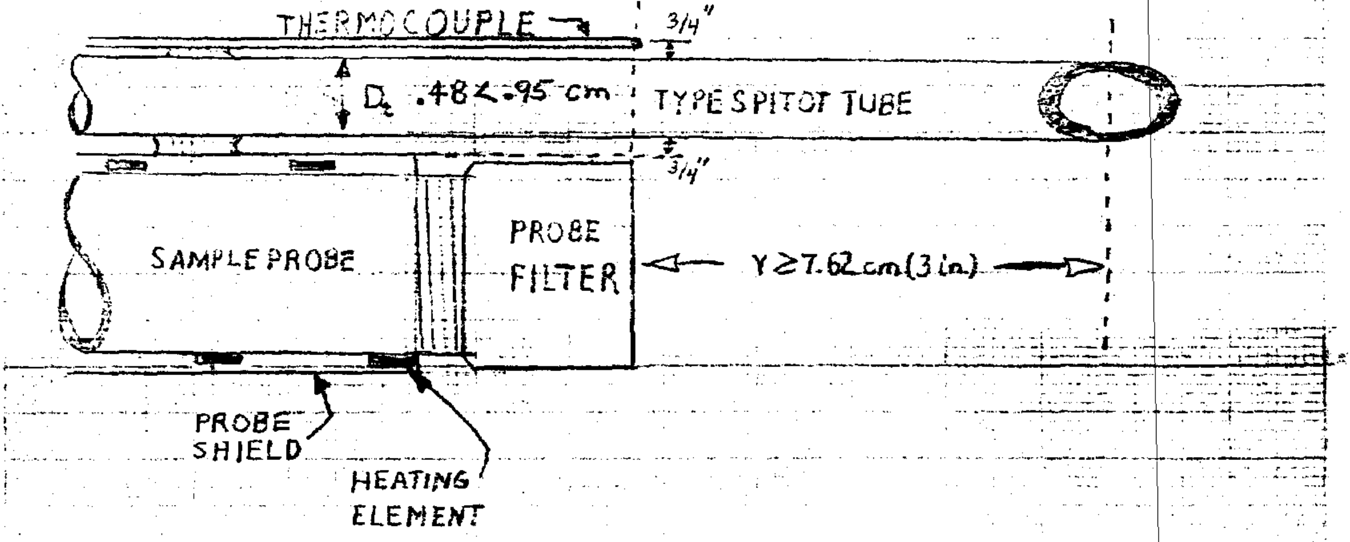

FIGURE 1-2

Example - SAMPLE TRAIN ASSEMBLY

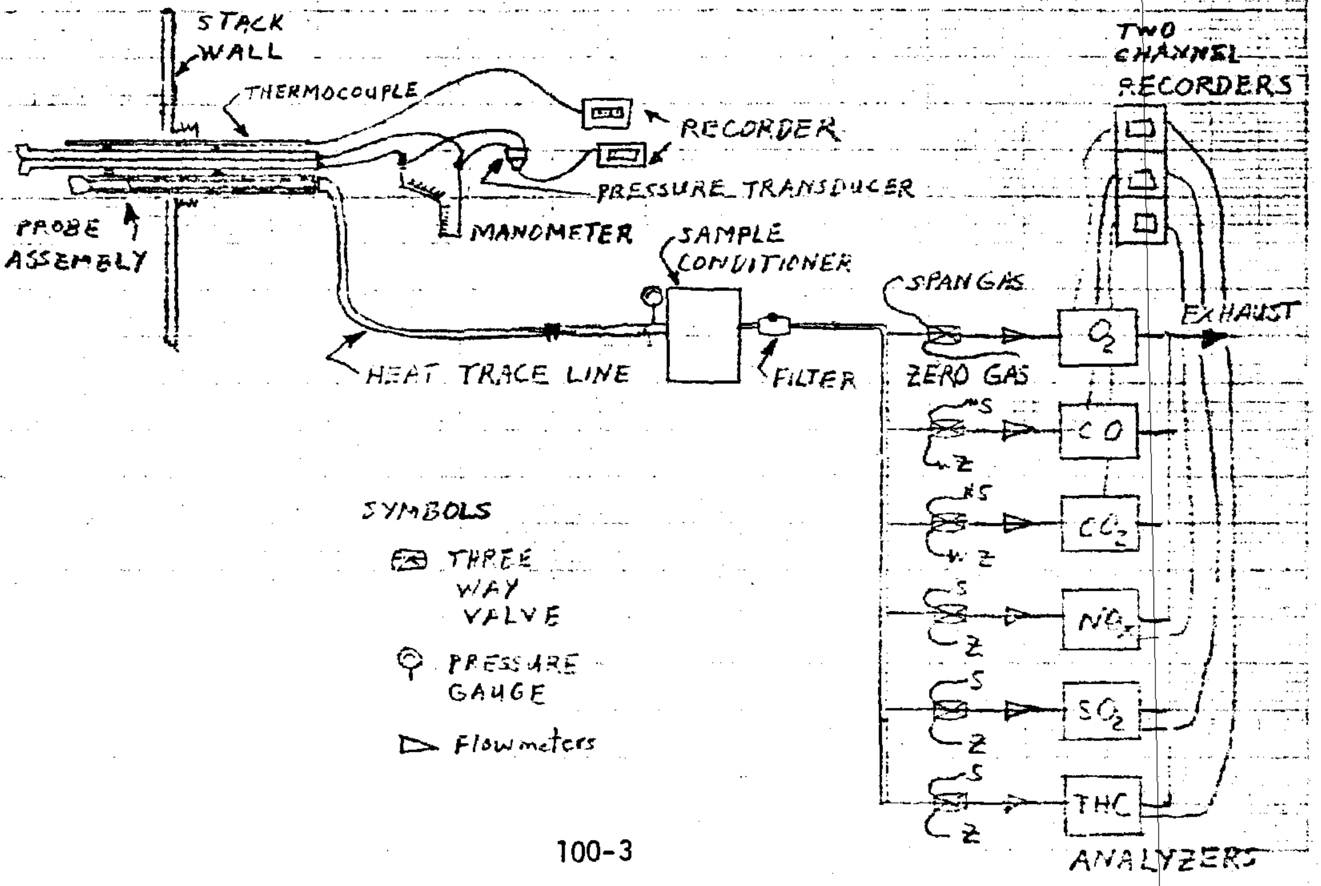

Figure 2

State of California

AIR RESOURCES BOARD

Engineering Evaluation Branch
Testing Section

SUMMARY OF TEST DATA

COMPANY: ______________________ ADDRESS: ______________________

POLLUTANT TESTED: __________ TEST METHOD: __________ ITEM TESTED: __________ TESTED BY: __________ DATE TESTED: __________

TIME	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
HOURLY AVG.																								
HIGH MIN. AVG:																								
NO. OF VIOLATIONS:																								
CORRECTED TO:																								
CONCENTRATIONS: SCALE:																								

REMARKS:

Figure 2

State of California

AIR RESOURCES BOARD

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SUMMARY OF TEST DATA

COMPANY: ____________________ ADDRESS: ____________________

POLLUTANT TESTED: __________ TEST METHOD: __________ ITEM TESTED: __________ TESTED BY: __________ DATE TESTED: __________

TIME	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
HOURLY AVG.																								
HIGH MIN. AVG:																								
NO. OF VIOLATIONS:																								
CORRECTED TO:																								
CONCENTRATIONS: SCALE:																								

REMARKS:

Alternatively, sample line made from other material (equivalent or better) may be used subject to the approval of the Control Agency's authorized representative.

2.1.4 Sample Conditioner: General specifications; filter, 90 percent efficient to 0.3 micron, glass fiber is acceptable; capable of reducing moisture content of sample to below the dewpoint 68°F (20°C); all parts, with the exception of the filter, exposed to the sample shall either be glass, stainless steel or teflon. Refrigeration type conditioners shall be equipped with a metal bellow or teflon lined diaphram pump capable of 40 cfh. . . Provisions shall be made for back flushing through the sample line from the sample conditioner through the probe for removing particulate buildup on the probe nozzle.

When sampling hydrocarbons C_3 and above it is recommended that heated line be used from the source to the hydrocarbon analyzer, that all filters be heated, and that no sample conditioning be performed that lowers sample temperature.

2.2 Carbon Dioxide and Carbon Monoxide: Nondispersive infrared analyzers are acceptable. See Table I for specifications.

2.3 Oxygen: A paramagnetic analyzer is acceptable. See Table I for specifications.

Table 1
ANALYZER SPECIFICATIONS FOR SOURCE SAMPLING

	Typical Principle of Operation 1/	Typical Range or Ranges PPM	Minimum Detectable Sensitivity PPM	Noise Level % of Full Scale (peak to peak)	Response Time Time Interval from a step Change in Input Conc. at Inlet to Instrument Output Reading of 90% of Steady State	Zero Drift Change in Instrument Output After 24 hours of Unadjusted Continuous Operation Change % of Full Scale	Calibration or Span Drift in Instrument After 24 Hours of Unadjusted Continuous Opert. Change % of Full Sale	Precision Maximum Ave. Deviation From Mean Change % of Full Sale	Operating Temperature or Range	Linearity Maximum % Deviation Between any Two Range Settings
Sulfur Dioxide	Photometric measurement of absorption of SO_2 radiation when subjected to ultraviolet light	0 – 300 0 – 3000	10	<± 1% HI Range <± 2% Lo Range	< 10 secs.	<± 1.	± 2.0	± 2% on all scales	0 to 50°C	± 1
Oxides of Nitrogen	Photometric measurement of the chemiluminescence from the reaction of NO with ozone	0 – 25 0 – 100 0 – 250 0 – 1000 0 – 2500	2	<± 1%	10 secs.	<± 1%	< 2.0	± 2% on all scales	0 to 50°C	± 1
Hydrogen Sulfide	Photometric measurement of the chemiluminescence from the reaction of of H_2S with ozone	0 – 5; 0 – 12.5 0 – 125 0 – 500 0 – 1250 0 – 5000	1	<±1%	< 10secs.	<± 1%	< 2.0	± 2% on all scales	0 to 50°C	± 1
Carbon Monoxide	Non-dispersive infra-red absorption	0 – 1000 0 – 5000	10	<± 1%	< 60 secs	<± 1%	<± 2.0	± 2% on all scales	0 to 50°C	± 1
Carbon Dioxide	Non-dispersive infra-red absorption	0 – 5% 0 – 50%	1% of instrument scale	<± 1%	< 60 secs	<± 1%	<± 2.0	± 2% on all scales	0 to 50°C	± 1
Hydrocarbons	Flame ionization method of detection	0 – 10 0 – 100 0 – 1000 0 – 10,000 0 - 100,000	1 to 2 ppm Methane	<± 1%	< 10	<± 1%	± 2	± 2% on all scales	0 – 60 °C	± 1
Oxygen	Uses the paramagnetic properties of oxygen	0 – 5% 0 – 10% 0 – 25%	.01%	<± 1%	< 60 secs.	<± 1%	± 2	± 1% of full scale	0 to 50°C	± 1

1/ Other types will also be acceptable.

Table 1
ANALYZER SPECIFICATIONS FOR SOURCE SAMPLING

	Typical Principle of Operation 1/	Typical Range or Ranges PPM	Minimum Detectable Sensitivity PPM	Noise Level % of Full Scale (peak to peak)	Response Time Time Interval from a step Change in Input Conc. at Inlet to Instrument Output Reading of 90% of Steady State	Zero Drift Change in Instrument Output After 24 hours of Unadjusted Continuous Operation Change % of Full Scale	Calibration or Span Drift in Instrument After 24 Hours of Unadjusted Continuous Opert. Change % of Full Sale	Precision Maximum Ave. Deviation From Mean Change % of Full Sale	Operating Temperature or Range	Linearity Maximum % Deviation Between a Two Range Settings
Sulfur Dioxide	Photometric measurement of absorption of SO_2 radiation when subjected to ultraviolet light	0 – 300 0 – 3000	30	<± 1% HI Range <± 2% Lo Range	< 10 secs.	<± 1.	± 2.0	± 2% on all scales	0 to 50°C	± 1
Oxides of Nitrogen	Photometric measurement of the chemiluminescence from the reaction of NO with ozone	0 – 25 0 – 100 0 – 250 0 – 1000 0 – 2500	2	<± 1%	10 secs.	<± 1%	< 2.0	± 2% on all scales	0 to 50°C	± 1
Hydrogen Sulfide	Photometric measurement of the chemiluminescence from the reaction of of H_2S with ozone	0 – 5; 0 – 12.5 0 – 125 0 – 500 0 – 1250 0 – 5000	1	<±1%	< 10secs.	<± 1%	< 2.0	± 2% on all scales	0 to 50°C	± 1
Carbon Monoxide	Non-dispersive infra-red absorption	0 – 1000 0 – 5000	10	<± 1%	< 60 secs	<± 1%	<± 2.0	± 2% on all scales	0 to 50°C	± 1
Carbon Dioxide	Non-dispersive infra-red absorption	0 – 5% 0 – 50%	1% of instrument scale	<± 1%	< 60 secs	<± 1%	<± 2.0	± 2% on all scales	0 to 50°C	± 1
Hydrocarbons	Flame ionization method of detection	0 – 10 0 – 100 0 – 1000 0 – 10,000 0 - 100,000	1 to 2 ppm Methane	<± 1%	< 10	<± 1%	± 2	± 2% on all scales	0 – 60°C	± 1
Oxygen	Uses the paramagnetic properties of oxygen	0 – 5% 0 – 10% 0 – 25%	.01%	<± 1%	< 60 secs.	<± 1%	± 2	± 1% of full scale	0 to 50°C	± 1

1/ Other types will also be acceptable.

2.4 Total Hydrocarbons: An analyzer using a flame ionization detector (FID) is acceptable. See Table I for specifications. (Note: The FID may not be acceptable for detecting certain organic compounds.)

2.5 Oxides of Nitrogen: An analyzer using chemiluminescent is acceptable. See Table I for specifications.

2.6 Sulfur Dioxide: An analyzer using ultraviolet absorption is acceptable. See Table I for specifications.

2.7 Other analyzers and measurement principles may be used, if their performance capability is equivalent to those referenced (see Q.A. Manual). An analyzer with more than a five percent interference from substances present in the sample stream (other than what is being measured) should not be used for the application.

2.8 Recorders: Shall be compatible with analyzers and employing strip chart paper with 100 divisions minimum.

2.9 Pitot tube. Same as required by Methods 1 and 2.

2.10 Differential pressure guage. Same as required by Methods 1 and 2.

2.11 For determining water moisture content the equipment shall be as specified by Method 4.

2.12 Barometer. Mercury, Aneroid, or other barometer capable of measuring atmosphereic pressure to within 2.5 mm Hg.

2.13 Vacuum guage. 760 mm Hg. guage, to be used for leak check of sampling train.

2.14 Thermocouple. Suitable for temperature range expected in the stack gases.

2.15 Calibration Gases

Zero Gas: Pure air or if appropriate nitrogen with less than 1 ppm of appropriate pollutant gas.

Span Gases: For each pollutant to be measured use one calibration gas in the expected concentration range. The calibration gas should be approximately 70 to 80 percent of the analyzer range and the expected maximum concentration to be measured should be no more than 90 percent of the range. The calibration gases used must be traceable to a primary standard (NBS standards if available).

3. Reagents

3.1 Distilled water: Distilled, deionized.

2.11 For determining water moisture content the equipment shall be as specified by Method 4.

2.12 Barometer. Mercury, Aneroid, or other barometer capable of measuring atmosphereic pressure to within 2.5 mm Hg.

2.13 Vacuum guage. 760 mm Hg. guage, to be used for leak check of sampling train.

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Span Gases: For each pollutant to be measured use one calibration gas in the expected concentration range. The calibration gas should be approximately 70 to 80 percent of the analyzer range and the expected maximum concentration to be measured should be no more than 90 percent of the range. The calibration gases used must be traceable to a primary standard (NBS standards if available).

3. Reagents

3.1 Distilled water: Distilled, deionized.

3.2 Acetone: Reagent grade

4. Preparation for Sampling

4.1 Cleaning of Sample Train: Thoroughly flush probe, heat trace line and sample conditioner with distilled water, followed by acetone, and dry with filtered dry air.

4.2 Continuous Analyzers: Allow analyzers to warm up according to manufacturer's instructions and performance check the analyzers in accordance with the manufacturers operator manual and conduct a zero and span check using a span gas of approximately 70 to 80 percent of the instrument range. Record data. The analyzer range should be selected such that the maximum concentration measured is no more than 90 percent of the range and the minimum concentration measured is no less than 30 percent of the range.

4.3 Sample Train Assembly: Assemble the sample train as shown in Figure 1.2. Lake check the vacuum side of the assembly (minus nozzle filter) to 15 inches of Hg. (guage). If the leak is equal to more than 0.20 CFH (94.ml/min) or is in excess of one percent of average sampling rate, check for leaks, correct any found and redo leak check. Repeat until a satisfactory result is obtained. Check pressure side of system with liquid Snoop or equivalent and correct any leaks. Alternate leak check methods are acceptable if they are equivalent or better than the specified method.

Sample train assembly can be modified to reflect actual stack conditions. Permissible modifications include: (1) If stack is at or below ambient temperature and there is no condensation problem, the heating element and sample conditioner can be eliminated. (2) If condensation in the probe itself is not a problem, the probe heating element can be eliminated. (3) If the only concern is with concentration, the pitot tube can be eliminated. (4) If stack temperature is uniform with time, the thermocouple can be eliminated.

5. Sampling

5.1 Select traverse points (only 1/3 number points, every third one, required as compared to particulate matter test Method 5) and determine moisture content and velocity pressures in the stack gases in accordance with Methods 1-1, 1-2 and 1-4. If sampling location meets criteria of eight diameters downstream and two diameters upstream of a disturbance and/or there is no reason to suspect stratification (stratification effects can be ignored if concentration variation is less than 10 percent) in the gas stream, select a convenient sampling point or a point at the point of average stack velocity (probe nozzle should never be within one inch of stack wall).

Sample train assembly can be modified to reflect actual stack conditions. Permissible modifications include: (1) If stack is at or below ambient temperature and there is no condensation problem, the heating element and sample conditioner can be eliminated. (2) If condensation in the probe itself is not a problem, the probe heating element can be eliminated. (3) If the only concern is with concentration, the pitot tube can be eliminated. (4) If stack temperature is uniform with time, the thermocouple can be eliminated.

5. Sampling

5.1 Select traverse points (only 1/3 number points, every third one, required as compared to particulate matter test Method 5) and determine moisture content and velocity pressures in the stack gases in accordance with Methods 1-1, 1-2 and 1-4. If sampling location meets criteria of eight diameters downstream and two diameters upstream of a disturbance and/or there is no reason to suspect stratification (stratification effects can be ignored if concentration variation is less than 10 percent) in the gas stream, select a convenient sampling point or a point at the point of average stack velocity (probe nozzle should never be within one inch of stack wall).

5.2 Turn on strip chart recorder so that hour coincides with division on strip chart (for one channel with dual pen recorders). Identify pollutant, source, range, calibration cylinder I.D. number, zero and span settings, chart speeds, date, time, person operating instruments on the chart, and any other pertinent data.

5.3 Insert sample probe assembly into stack and block-off remainer of opening. Set probe at predetermined position and note on strip charts. If traverse is required, leave probe in position for three to five minutes (allow enough time for system to be flushed and instruments to respond fully). Move probe to next position and repeat. Continue until stack has been fully traversed. Record data on summary sheet (Figure 100-3). From data, select point of average concentration and/or velocity. Set probe at this point.

5.4 With probe at average point, sample for desired time period without further adjustments. Sampling should be conducted for a minimum of two hours. Conduct zero and span checks every hour, adjust settings as necessary, mark strip charts and record in log books. When zero and span checks repeat within one percent, make checks every six hours. As necessary back flush through probe every two hours to prevent particulate build-up on probe filter. The strip chart should be marked to indicate time on an hourly basis.

At end of sample period, make final zero and span check and mark charts and record data. If velocity at end of test is 50 percent different from at start or concentrations have changed by 100 percent, repeat traverse as indicated in 5.3.

5.5 Repeat leak check. If leak rate is two percent or more of total sample flow (approximately 0.8 CFH) discard test.

6. Calculations

6.1 Emission Rate, lbs/hr. lbs of Pollutant/Hr. =

$$(PPM)\left(\frac{M}{385 \times 10^6}\right)(Q)\ (60) = PPM \times M \times Q \times 1.56 \times 10^{-7}$$

Where: M = molecular weight - lb/lb mole.

385×10^6 = Constant

Q = standard dry cubic feet per minute of stack effluents

$$Q = Qs \times \frac{Tstd\ Ps}{Ts\ Pstd}\ (1 - Bws) = Qs\left(\frac{528}{Ts}\right)\left(\frac{Ps}{29.92}\right)\ (1 - Bws)$$

$$= 17.65\ \frac{Qs\ Ps}{Ts}\ (1 - Bws)$$

B_{ws} = percent water vapor in effluent stream

SUBSCRIPTS

s = stack conditions

std - standard condition

6.2 Percent Excess Air (EA)

At end of sample period, make final zero and span check and mark charts and record data. If velocity at end of test is 50 percent different from at start or concentrations have changed by 100 percent, repeat traverse as indicated in 5.3.

5.5 Repeat leak check. If leak rate is two percent or more of total sample flow (approximately 0.8 CFH) discard test.

6. Calculations

6.1 Emission Rate, lbs/hr. lbs of Pollutant/Hr. =

$$(PPM) \left(\frac{M}{385 \times 10^6}\right) (Q) \quad (60) = PPM \times M \times Q \times 1.56 \times 10^{-7}$$

Where: M = molecular weight - lb/lb mole.

385×10^6 = Constant

Q = standard dry cubic feet per minute of stack effluents

$$Q = Qs \times \frac{Tstd\ Ps}{Ts\ Pstd} \ (1 - Bws) = Qs \left(\frac{528}{Ts}\right) \left(\frac{Ps}{29.92}\right) \ (1 - Bws)$$

$$= 17.65 \ \frac{Qs\ Ps}{Ts} \ (1 - Bws)$$

B_{ws}= percent water vapor in effluent stream

SUBSCRIPTS

s = stack conditions

std - standard condition

6.2 Percent Excess Air (EA)

$$\% EA = \left[\frac{\%O_2 - 0.5\% CO}{0.264 \ \%N_2 - (\%O_2 - 0.5\% CO)} \right] 100$$

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

$\%CO$ = Percent CO by volume (dry basis)

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

.264 = Ratio of O_2 to N_2 in air v/v

6.3 Pollutant Concentration Calculated to 12% CO_2 or 3% O_2

For 12% CO_2:

$$\underset{(12\% \ CO_2)}{\text{Conc}} = \underset{(\text{Std.})}{\text{Conc.}} \times \frac{12\%}{\% \ CO_2 \text{ during test (dry basis)}}$$

For 3% O_2 using O_2 in air as 20.9%

$$\underset{(3\% \ O_2)}{\text{Conc.}} = \underset{(\text{std.})}{\text{Conc.}} \times \frac{20.9 \times 3.0}{20.9 - \%O_2 \text{ during test (dry basis)}}$$

7.0 Calibrations

All calibrations are to be performed in accordance with the Air Resources Board "Source Testing Quality Assurance and Quality Control Manual Vol. VI."

195S/033H

METHOD 1-104 - REFERENCE METHOD FOR DETERMINATION OF BERYLLIUM EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability:

1.1 Principle: Beryllium emissions are isokinetically sampled from the source, and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry.

1.2 Applicability: This method is applicable for the determination of beryllium emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

2. Apparatus:

2.1 Sampling Train. A schematic of the sampling train used by EPA is shown in Figure 104-1. Commercial models of this train are available, although construction details are described in APTD-0581,[1] and operating and maintenance procedures are described in APTD-0576. The components essential to this sampling train are the following:

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[1] These documents are available for a nominal cost from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22151.

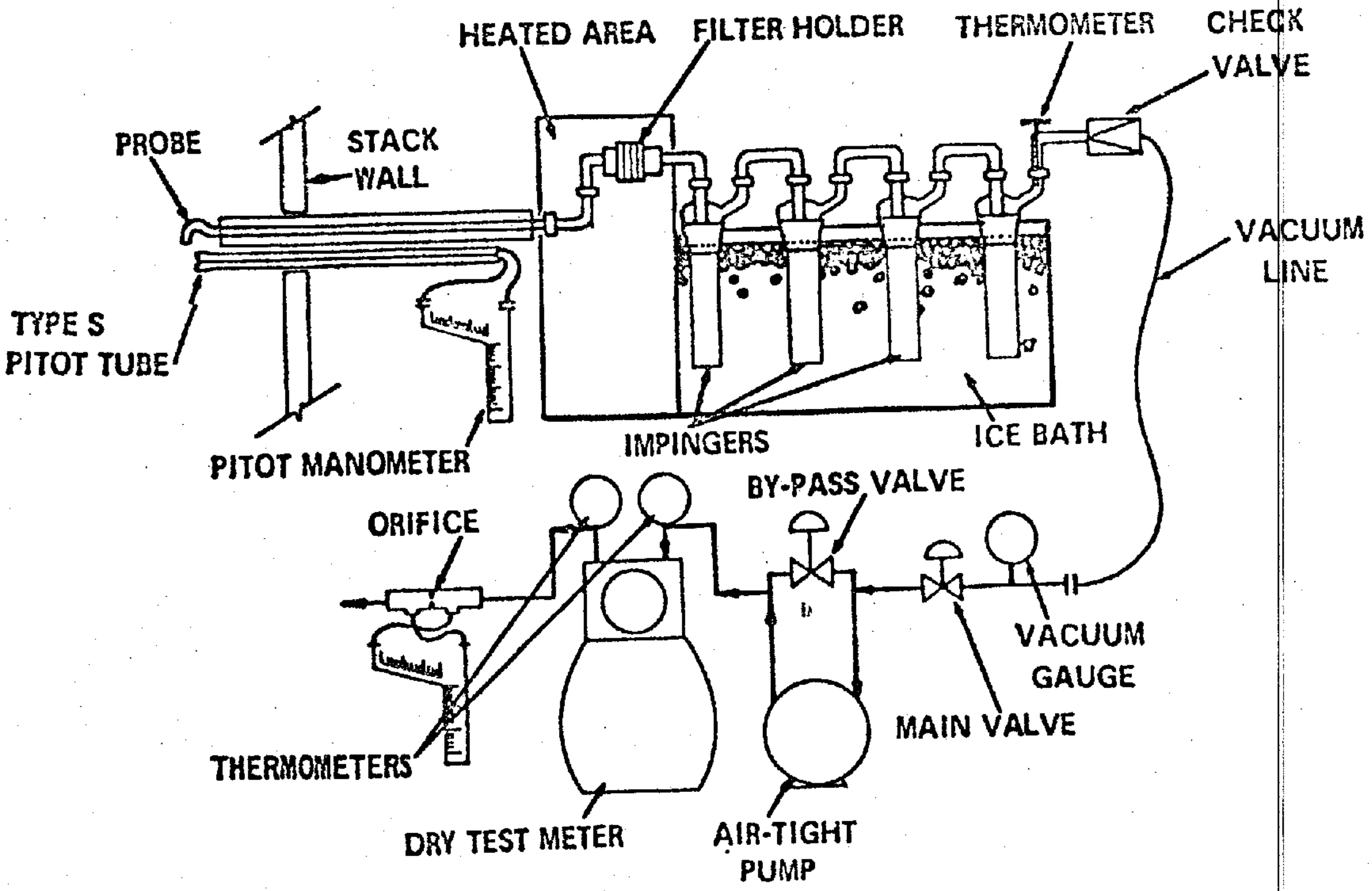

Figure 104-1. Beryllium sampling train

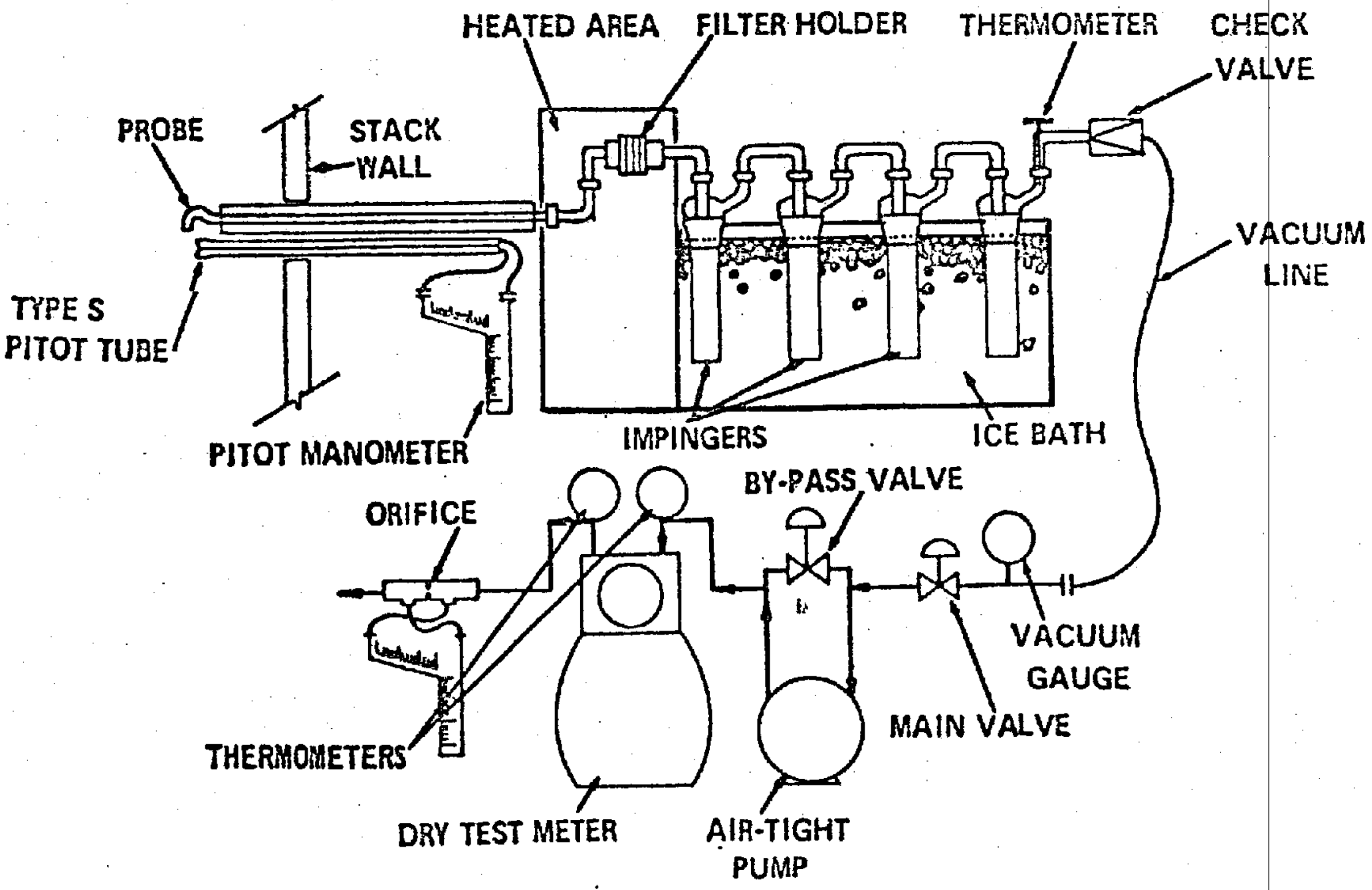

Figure 104-1. Beryllium sampling train

2.1.1 Nozzle. Stainless steel or glass with sharp, tapered leading edge.

2.1.2 Probe. Sheathed Pyrex[2/] glass. A heating system capable of maintaining a minimum gas temperature in the range of the stack temperature at the probe outlet during sampling may be used to prevent condensation from occurring.

2.1.3 Pitot tube. Type S (Figure 104-2), or equivalent, with a coefficient within 5 percent over the working range, attached to probe to monitor stack gas velocity.

2.1.4 Filter holder. Pyrex glass. the filter holder must provide a positive seal against leakage from outside or around the filter. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

2.1.5 Impingers. Four Greenburg-Smith impingers connected in series with glass ball joint fittings. The first, third and fourth impingers may be modified by replacing the tip with a 1/2 inch l.d. glass tube extending to one-half inch from the bottom of the flask.

[2/] Mention of trade names on specific products does not constitute endorsement by the Air Resources Board.

2.1.6 Metering Systems. Vacuum gauge, leakless pump, thermometers capable of measuring temperature to within 5°F, dry gas meter with 2 percent accuracy, and related equipment, described in APTD-0581, to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer. To measure atmospheric pressure to ± 0.1 in Hg.

2.2 Measurement of stack conditions (stack pressure, temperature, moisture and velocity).

2.2.1 Pitot tube: Type S, or equivalent, with a coefficient within 5 percent over the working range.

2.2.2 Differential Pressure Gauge. Inclined manometer, or equivalent, to measure velocity head to within 10 percent of the minimum value.

2.2.3 Temperature gauge. Any temperature measuring device to measure stack temperature to within 5°F.

2.2.4 Pressure gauge. Pitot tube and inclined manometer, or equivalent, to measure stack pressure to within 0.1 in Hg.

2.2.5 Moisture determination. Wet and dry bulb therometers, drying tubes, condensers, or equivalent, to determine stack gas moisture content to within 1 percent.

2.3 Sample recovery.

2.3.1 Probe cleaning rod. At least as long as probe.

2.3.2 Leakless glass sample bottles. 500 ml.

2.3.3 Graduated cylinder. 250 ml.

2.3.4 Plastic jar. Approximately 300 ml.

2.4 Analysis

2.4.1 Atomic absorption spectrophotometer. To measure absorbance at 234.8 nm. Perkin Elmer Model 303, or equivalent, with N_2O/acetylene burner.

2.4.2 Hot plate.

2.4.3 Perchloric acid fume hood.

3. Reagents.

3.1 Stock reagents.

3.1.1 Hydrochloric acid concentrated

3.1.2 Perchloric acid. Concentrated, 70 percent.

3.1.3 Nitric acid. Concentrated.

2.3 Sample recovery.

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3.1 Stock reagents.

3.1.1 Hydrochloric acid concentrated

3.1.2 Perchloric acid. Concentrated, 70 percent.

3.1.3 Nitric acid. Concentrated.

3.1.4 Sulfuric Acid. Concentrated

3.1.5 Distilled and deionized water.

3.1.6 Beryllium powder. 98 percent minimum purity.

3.2 Sampling

3.2.1 Filter. Millipore AA, or equivalent. It is suggested that a Whatman 41 filter be placed immediately against the back side of the millipore filter as a guard against breaking the Millipore filter. In the analysis of the filter, the Whatman 41 filter should be included with the Millipore filter.

3.2.2 Silica gel. Indicating type, 6 to 16 mesh, dried at 350° F for 2 hours.

3.2.3 Distilled and deionized water.

3.3 Sample recovery

3.3.1 Distilled and deionized water.

3.3.2 Acetone. Reagent grade.

3.3.3 Wash acid. 1.1 V/V hydrochloric acid-water

3.4 Analysis.

3.4.1 Sulfuric acid solution, 12 N. Dilute 333 ml of concentrated sulfuric acid 1 to 1 with distilled water.

3.4.2 25 percent V/V hydrochloric acid-water.

3.5 Standard Beryllium Solution

3.5.1 Stock Solution. 1 ug/ml beryllium. Dissolve 10 mg of beryllium in 80 ml of 12 N sulfuric acid solution and dilute to a volume of 1000 ml with distilled water. Dilute a 10 ml aliquot to 100 ml with 25 percent v/v hydrochloric acid, giving a concentration of 1 ug/ml. This dilute stock solution should be prepared fresh daily. Equivalent strength (in beryllium) stock solutions may be prepared from beryllium salts as $BeCl_2$ and $BE(NO_3)_2$ (98 percent minimum purity).

4. Procedure.

4.1 Guidelines for source testing are detailed in the following sections. These guidelines are generally applicable; however, most sample sites differ to some degree and temporary alterations such as stack extensions or expansions often are required to insure the best possible sample site. Further, since beryllium is hazardous, care should be taken to minimize exposure. Finally, since the total quantity of beryillium to be collected is quite small, the test must be carefully conducted to prevent contamination or loss of sample.

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4.2 Selection of a sampling site and minimum number of traverse points.

4.2.1 Select a suitable sampling site that is as close as practicable to the point of atmospheric emission. If possible stacks smaller than 1 foot in diameter from the following equation:

$$D_e = \frac{2LW}{L + W} \qquad \text{eq. 104-1}$$

where:

D_e = equivalent diameter

L = length

W = Width

4.2.3 When the above sampling site criteria can be met, the minimum number of traverse points is four (4) for stacks 1 foot in diameter or less, eight (8) for stacks larger than 1 foot but 2 feet in diameter or less, and twelve (12) for stacks larger than 2 feet.

4.2.4 Some sampling situations may render the above sampling site criteria impractical. When this is the case choose a convenient sampling location and use Figure 104-3 to determine the minimum number of traverse points. However, use Figure 104-3 only for stacks 1 foot in diameter or larger.

4.2.5 To use Figure 104-3, first measure the distance from the chosen sampling location to the nearest upstream and downstream disturbances. Divide this distance by the diameter or equivalent diameter to determine the distance in terms of pipe diameters. Determine the corresponding number of traverse points for each distance from Figure 104-3. Select the higher of the two numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of four, and for rectangular stacks the number follows the criteria of Section 4.3.2.

4.2.6 If a selected sampling point is closer than 1 inch from the stack wall, adjust the location of that point to ensure that the sample is taken at least 1 inch away from the wall.

4.3 Cross-sectional layout and location of traverse points.

4.3.1 For circular stacks locate the traverse points on at least two diameters according to Figure 104-4 and Table 104-1. The traverse axes shall divide the stack cross sections into equal parts.

4.3.2 For rectangular stacks divide the cross section into as many equal rectangular areas as traverse points, such that the ratio of the length to the width of the elemental areas is between 1 and 2. Locate the traverse points at the centroid of each equal area according to Figure 104-5.

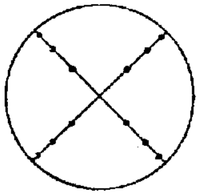


Figure 102-4. Cross section of circular stack showing location of traverse points on perpendicular diameters.

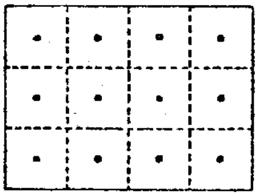


Figure 102-5. Cross section of rectangular stack divided into 12 equal areas, with traverse points at centroid of each area.

TABLE 104-1—LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS

[Percent of stack diameter from inside wall to traverse point]

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	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												96.9
24												98.9

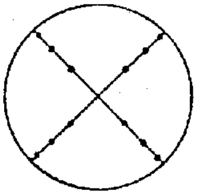
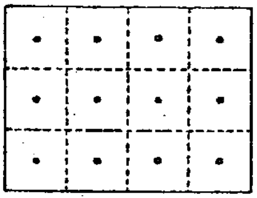


Figure 102-4. Cross section of circular stack showing location of traverse points on perpendicular diameters.



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1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.8	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.5	73.9	67.0
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										95.1	91.3	86.8
20										98.7	94.0	89.5
21											95.5	92.1
22											98.9	94.5
23												96.8
24												98.9

4.4 Measurement of stack conditions.

4.4.1 Set up the apparatus as shown in Figure 104-2. Make sure all connections are tight and leak free. Measure the velocity head and temperature at the traverse points specified by Section 4.2 and 4.3.

4.4.2 Measure the static pressure in the stack.

4.4.3 Determine the stack gas moisture.

4.4.4 Determine the stack gas molecular weight from the measured moisture content and knowledge of the expected gas stream composition. A standard Orsat analyzer has been found valuable at combustion sources. In all cases, sound engineering judgment should be used.

4.5 Preparation of a sampling train.

4.5.1 Prior to assembly, clean all glassware (probe, impingers, and connectors) by soaking in wash acid for 2 hours. Place 100 ml of distilled water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g of preweighted silica gel in the fourth impinger. Save a portion of the distilled water as a blank in the sample analysis. Set up the train and the probe as in Figure 104-1.

4.5.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sampling rate. If condensation in the probe or filter is a problem, probe and filter heaters will be required. Adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 225° F. If the stack gas is in excess of about 200° F, consideration should be given to an alternative procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. Place crushed ice around the impingers. Add more ice during the test to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.6 Beryllium train operation.

4.6.1 For each run, record the data required on the example sheet shown in Figure 104-6. Take readings at each sampling point at least every 5 minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate.

4.6.2 Sample at a rate of 0.5 to 1.0 $ft.^3/min$. Samples shall be taken over such a period or periods as are necessary to accurately determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, 4.5.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sampling rate. If condensation in the probe or filter is a problem, probe and filter heaters will be required. Adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 225° F. If the stack gas is in excess of about 200° F, consideration should be given to an alternative procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. Place crushed ice around the impingers. Add more ice during the test to keep the temperature of the gases leaving the last impinger at 70° F. or less.

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PLANT ____________
LOCATION ____________
OPERATOR ____________
DATE ____________
RUN NO. ____________
SAMPLE BOX NO. ____________
METER BOX NO. ____________
METER $\Delta H_@$ ____________
C FACTOR ____________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE ________
BAROMETRIC PRESSURE ________
ASSUMED MOISTURE, % ________
HEATER BOX SETTING ________
PROBE LENGTH, m. ________
NOZZLE DIAMETER, in. ________
PROBE HEATER SETTING ________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_S), in. Hg.	STACK TEMPERATURE (T_S), °F	VELOCITY HEAD (ΔP_S),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (Vm), ft^3	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
							INLET (Tm_{in}), °F	OUTLET (Tm_{out}), °F		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 104-6. Field data

sufficient tests shall be made so as to allow accurate determination or calculation of the emissions which will occur over the duration of the cycle. A minimum sample time of 2 hours is recommended.

4.6.3 To begin sampling, 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. Sample for at least 5 minutes at each, traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs which aid in the rapid adjustment of the sampling rate without other computations are in APTD-0576 and are available from commercial suppliers. Note that standard monographs are applicable only for Type S pitot tubes and air or a stack gas with an equivalent density. Contact ARB or the sampling train supplier for instructions when the standard nonograph is not applicable.

4.6.4 Turn off the pump at the conclusion of each run and record the final readings. Immediately remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in Section 4.7.

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4.7 Sample Recovery.

4.7.1 (All glass storage bottles and the graduated cylinder must be precleaned as in 4.5.1.) This operation should be performed in an area free of possible beryllium contamination. When the sampling train is moved, care must be exercised to prevent breakage and contamination.

4.7.2 Disconnect the probe from the impinger train. Remove the filter and any loose particulate matter from the filter holder and place in a sample bottle. Place the contents (measured to ±1 ml) of the first three impingers into another sample bottle. Rinse the probe and all glassware between it and the back half of the third impinger with water and acetone, and add this to the latter sample bottle. Clean the probe with a brush or a long slender rod and cotton balls. Use acetone while cleaning. Add these to the sample bottle. Retain a sample of the water and acetone as a blank. The total amount of wash water and acetone used should be measured for accurate blank correction. Place the silica gel in the plastic jar. Seal and secure all sample containers for shipment. If an additional test is desired, the glassware can be carefully double rinsed with distilled water and reassembled. However, if the glassware is to be out of use more than 2 days, the initial acid wash procedure must be followed.

4.8 Analysis

4.8.1 Apparatus preparation. Clean all glassware according to the procedure of Section 4.5.1. Adjust the instrument settings according to the instrument manual, using an absorption wavelength of 234.8 nm.

4.8.2 Sample preparation. The digestion of beryllium samples is accomplished in part in concentrated perchloric acid. Caution: The analyst must insure that the sample is heated to light brown fumes after the initial nitric acid addition; otherwise, dangerous perchlorates may result from the subsequent perchloric acid digestion. Perchloric acid also should be used only under a perchloric acid hood.

4.8.2.1 Transfer the filter and any loose particulate matter from the sample container to a 150 ml beaker. Add 35 ml concentrated nitric acid. Heat on a hotplate until light brown fumes are evident to destroy all organic matter. Cool to room temperature and add 5 ml concentrated sulfuric acid and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4

4.8.2.2 Place a portion of the water and acetone sample into a 150 ml beaker and put on a hotplate. Add portions of the remainder as evaporation proceeds and

4.8 Analysis

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4.8.2.1 Transfer the filter and any loose particulate matter from the sample container to a 150 ml beaker. Add 35 ml concentrated nitric acid. Heat on a hotplate until light brown fumes are evident to destroy all organic matter. Cool to room temperature and add 5 ml concentrated sulfuric acid and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4

4.8.2.2 Place a portion of the water and acetone sample into a 150 ml beaker and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness. Cool the residue and add 35 ml concentrated nitric acid. Heat on a hotplate until light brown fumes are evident to destroy any organic matter. Cool to room temperature and add 5 ml concentrated sulfuric acid, and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4.

4.8.2.3 Weigh the spent silica gel and report to the nearest gram.

4.8.2.4 Samples from 4.8.2.1 and 4.8.2.2 may be combined here for ease of analysis. Replace on a hotplate and evaporate to dryness in a perchloric acid hood. Cool and dissolve the residue in 10.0 ml of 25 percent V/V hydrochloric acid. Samples are now ready for the atomic absorption unit. The beryllium concentration of the sample must be within the calibration range of the unit. If necessary, further dilution of sample with 25 percent V/V hydrochloric acid must be performed to bring the sample within the calibration range.

4.8.3 Beryllium determination. Analyze the samples prepared in 4.8.2 at 234.8 nm using a nitrous oxide/acetylene flame. Aluminum, silicon and other elements can interfere with this method if present in large quantities. Standard methods are available, however, to effectively eliminate these interferences (see Reference 5).

5. Calibration

5.1 Sampling Train.

5.1.1 Use standard methods and equipment as detailed in APTD-0576 to calibrate the rate meter, pitot tube, dry gas meter and probe heater (if used). Recalibrate prior to each test series.

5.2 Analysis

5.2.1 Standardization is made with the procedure as suggested by the manufacturer with standard beryllium solution. Standard solutions will be prepared from the stock solution by dilution with 25 percent V/V hydrochloric acid. The linearity of working range should be established with a series of standard solutions. If collected samples are out of the linear range, the samples should be diluted. Standards should be interspersed with the samples since the calibration can change slightly with time.

6. Calculations

6.1 Average dry gas meter temperature, stack temperature, stack pressure and average orifice pressure drop. See data sheet (Figure 104-6).

method if present in large quantities. Standard methods are available, however, to effectively eliminate these interferences (see Reference 5).

5. Calibration

5.1 Sampling Train.

5.1.1 Use standard methods and equipment as detailed in APTD-0576 to calibrate the rate meter, pitot tube, dry gas meter and probe heater (if used). Recalibrate prior to each test series.

5.2 Analysis

5.2.1 Standardization is made with the procedure as suggested by the manufacturer with standard beryllium solution. Standard solutions will be prepared from the stock solution by dilution with 25 percent V/V hydrochloric acid. The linearity of working range should be established with a series of standard solutions. If collected samples are out of the linear range, the samples should be diluted. Standards should be interspersed with the samples since the calibration can change slightly with time.

6. Calculations

6.1 Average dry gas meter temperature, stack temperature, stack pressure and average orifice pressure drop. See data sheet (Figure 104-6).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to stack conditions by using equation 104-2.

$$V_{m_s} = V_m \frac{T^{s}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_s} \qquad \text{eq. 104-2}$$

where:

V_{m_s} = Volume of gas sample through the dry gas meter (stack conditions). ft^3

V_m = Volume of gas sample through the dry gas meter (meter conditions). ft^3

T_s = Average temperature of stack gas, ^{o}R

T_m = Average dry gas meter temperature, ^{o}R

p_{bar} = Barometric pressure at the orifice meter, in Hg.

H = Average pressure drop across the orifice meter, in H_2O.

13.6 = Specify gravity of mercury.

P_s = Stack pressure, $p_{bar} \pm$ static pressure, in Hg.

6.3 Volume of water vapor.

$$V_{w_s} = K_w V_{i_s} \frac{T_s}{P_s} \qquad \text{eq. 104-3}$$

Where:

V_{w_s} = Volume of water vapor in the gas sample (stack conditions), ft^3.

K_w = $0.00267 \frac{\text{inHg-ft}^3}{\text{m}/^{o}\text{R}}$, when these units are used

V_{i_s} = Total volume of liquid collected in impingers and silica gel (see Figure 104-7), ml.

T_s = Average stack gas temperature, ^oR

P_s = Stack pressure, P_{bar} ($\pm$ static pressure, in Hg.)

6.4 Total gas volume.

$$V_{total} = V_{m_s} + V_{w_s} \qquad \text{eq. 104-4}$$

Where:

V_{total} = Total volume of gas sample (stack condition), ft^3.

V_{m_s} = Volume of gas through dry gas meter (stack conditions), ft^3.

V_{w_s} = Volume of water vapor in gas sample (stack conditions), ft^3.

6.5 Stack gas velocity.

Use equation 104-5 to calculate the stack gas velocity.

$$(V_s)_{avg} = K_p C_p \; (\quad p)_{avg} \quad \frac{(T_s)_{avg}}{P_s M_s}$$

eq. 104-5

where:

$(V_s)avg$ = Average stack gas velocity, feet per second

K_p = $85.39 \, \frac{ft}{sec} \left(\frac{lb\text{-}inHg}{lb\ mole\text{-}^oR\text{-}inH_2O} \right)^{1/2}$, when these units are used.

C_p = Pitot tube coefficient, dimensionless.

(T_s) avg. = Average stack gas temperature, ^oR.

(p) avg. = Average square root of the velocity head of stack gas $(in\ H_2O)^{1/2}$ (see Figure 104-8).

P_s = Stack pressure, $P_{bar} \pm$ static pressure, in Hg.

T_s = Average stack gas temperature, ^{o}R

P_s = Stack pressure, P_{bar} (± static pressure, in Hg.)

6.4 Total gas volume.

$$V_{total} = V_{m_s} + V_{w_s} \qquad \text{eq. 104-4}$$

Where:

V_{total} = Total volume of gas sample (stack condition), ft^3.

V_{m_s} = Volume of gas through dry gas meter (stack conditions), ft^3.

V_{w_s} = Volume of water vapor in gas sample (stack conditions), ft^3.

6.5 Stack gas velocity.

Use equation 104-5 to calculate the stack gas velocity.

$$(V_s)_{avg} = K_pC_p(\quad p)_{avg} \quad \frac{(T_s)_{avg}}{P_sM_s}$$

eq. 104-5

where:

$(V_s)avg$ = Average stack gas velocity, feet per second

K_p = $85.39 \frac{ft}{sec} \left(\frac{lb\text{-}inHg}{lb\ mole\text{-}^{o}R\text{-}inH_2O}\right)^{1/2}$, when these units are used.

C_p = Pitot tube coefficient, dimensionless.

(T_s) avg. = Average stack gas temperature, ^{o}R.

$(\quad p)$ avg. = Average square root of the velocity head of stack gas $(in\ H_2O)^{1/2}$ (see Figure 104-8).

P_s = Stack pressure, P_{bar} ± static pressure, in Hg.

M_s = Molecular weight of stack gas (wet basis), the summation of the products of the molecular weight of each component multiplied by its volumetric proportion in the mixture, lb/lb. mole.

Figure 104-8 shows a sample recording sheet for velocity traverse data. Use the averages in the last two columns of Figure 104-8 to determine the average stack gas velocity from equation 104-5.

6.6 Beryllium collected. Calculate the total weight of beryllium collected by using equation 104-6.

$$W_t = V_1C_1 - V_wC_w - V_aC_a$$

eq. 104-6

where:

W_t = Total weight of beryllium collected, ug.

V_t = Total volume of hydrochloric acid from step 4.8.2.4, ml.

C_t = Concentration of beryllium found in sample, ug/ml.

V_w = Total volume of water used in sampling (impinger contents plus all wash amounts), ml.

C_w = Blank concentration of beryllium in water, ug/ml.

PLANT____________________

DATE____________________

RUN NO.____________________

STACK DIAMETER, in.____________________

BAROMETRIC PRESSURE, in. Hg.____________________

STATIC PRESSURE IN STACK (P_g), in. Hg.__________

OPERATORS____________________

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Velocity head, in. H_2O	$\sqrt{\Delta_p}$	Stack Temperature (T_S), °F
	AVERAGE:		

Figure 104-8. Velocity traverse data.

PLANT__________________________________

DATE__________________________________

RUN NO.________________________________

STACK DIAMETER, in._______________________

BAROMETRIC PRESSURE, in. Hg._________________

STATIC PRESSURE IN STACK (P_g), in. Hg.__________

OPERATORS______________________________

SCHEMATIC OF STACK
CROSS SECTION

Traverse point number	Velocity head, in. H_2O	$\sqrt{\Delta_p}$	Stack Temperature (T_S), °F
	AVERAGE:		

Figure 104-8. Velocity traverse data.

V_a = Total volume of acetone used in sampling (impinger contents plus all).

C_a = Blank concentration of beryllium in acetone, ug/ml.

6.7 Total beryllium emissions. Calculate the total amount of beryllium emitted from each stack per day by equation 104-7. This equation is applicable for continuous operations. For cyclic operations, use only the time per day each stack is in operation. The total beryllium emissions from a source will be the summation of results from all stacks.

$$R = W_t (V_s)_{avg} A_s / V_{total} \times 86{,}400 \text{ seconds/day}/10^6 \text{ ug/g} \qquad \text{eq. 104-7}$$

where:

R = Rate of emission, g/day.

W_t = Total weight of beryllium collected, ug.

V_{total} = Total volume of gas sample (stack conditions), ft^3.

$(V_s)_{avg}$ = Average stack gas velocity, feet per second.

A_s = Stack area, ft^2.

6.8 Isokinetic variation (comparison of velocity of gas in probe tip to stack velocity).

$$I = 100\ V_{total}/A_n\Theta/(VS)_{avg} \qquad \text{eq. 104-8}$$

where:

I = Percent of isokinetic sampling.

V_{total} = Total volume of gas sample (stack conditions) ft^3.

A_n = Probe tip area, ft^2

θ = Sampling time, sec.

$(V_s)_{avg}$ = Average stack gas velocity, feet per second.

7. Evaluation of results.

7.1 Determination of compliance.

7.1.1 Each performance test shall consist of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, the average of results of all repetitions shall apply.

7.2 Acceptable isokinetic results.

7.2.1 The following range sets the limit on acceptable isokinetic sampling results:

If 90 percent $< I <$ 110 percent, the results are acceptable; otherwise, reject the test and repeat.

where:

I = Percent of isokinetic sampling.

V_{total} = Total volume of gas sample (stack conditions) ft^3.

A_n = Probe tip area, ft^2

θ = Sampling time, sec.

$(V_s)_{avg}$ = Average stack gas velocity, feet per second.

7. Evaluation of results.

7.1 Determination of compliance.

7.1.1 Each performance test shall consist of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, the average of results of all repetitions shall apply.

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METHOD 106 - DETERMINATION OF VINYL CHLORIDE EMISSIONS FROM STATIONARY SOURCES

Introduction

Performance of this method should not be attempted by persons unfamilar with the operation of a gas chromatograph, nor by those who are unfamilar with source sampling, as there are many details that are beyond the scope of this presentation. Case must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Principle and Applicability

   1.1 An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis, using a flame ionization detector.

   1.2 The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter.

2. Range and Sensitivity. The lower limit of detection will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg.

3. Interferences. Acetaldehyde, which can occur in some vinyl chloride sources, will interfere with the vinyl chloride peak from the Chromasorb 102[1] column. See Sections 4.3.2 and 6.4. If resolution of the vinyl chloride peak is still not satisfactory for a particular sample, then

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[1] Mention of trade names on specific products does not constitute endorsement by the Air Resources Board.

chromatograph parameters can be further altered with prior approval of the Executive Officer. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

4. Apparatus

4.1 Sampling (Figure 106-1).

4.1.1 Probe. Stainless Steel, Pyrex glass, or Teflon Tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample line. Teflon, 6.4 mim. outside diameter, of sufficient length at connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick-connects, with ball checks (one pair without) located as shown in Figure 106-1.

4.1.4 Tedlar bags, 100 liter capacity. To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collections.

4.1.5 Rigid leakproof containers for 4.1.4 with covering to protect contents from sunlight.

4.1.6 Needle valve. To adjust sample flow rate.

chromatograph parameters can be further altered with prior approval of the Executive Officer. If alteration of the chromatograph parameters fails to resolve the vinyl chloride peak, then supplemental confirmation of the vinyl chloride peak through an absolute analytical technique, such as mass spectroscopy, must be performed.

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4.1.4 Tedlar bags, 100 liter capacity. To contain sample. Teflon bags are not acceptable. Aluminized Mylar bags may be used, provided that the samples are analyzed within 24 hours of collections.

4.1.5 Rigid leakproof containers for 4.1.4 with covering to protect contents from sunlight.

4.1.6 Needle valve. To adjust sample flow rate.

4.1.7 Pump. Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube. To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter. For observing sample flow rate: capable of measuring a flow range from 0.10 to 1.00 liter per minute.

4.1.10 Connecting tubing. Teflon, 6.4 mm outside diameter to assembly sample train (Figure 106-1).

4.1.11 Pitot tube. Type S (or equivalent), attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity.

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis

4.3.1 Gas chromatograph. With flame ionization detector, potentiometric strip chart recorder and 1.0 to 5.0 ml heated sampling loop in automatic sample valve.

4.3.2 Chromatographic column. Stainless steel, 2 m x 3.2 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SF-96, 20 percent on 60/80 mesh AW Chromasorb P, stainless steel, 2 m x 3.2 mm or Porapak T, 80/100 mesh, stainless steel, 1 m x 3.2 mm is required if

4.1.7 Pump. Leak-free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal tube. To prevent admission of vinyl chloride to atmosphere in vicinity of samplers.

4.1.9 Flow meter. For observing sample flow rate: capable of measuring a flow range from 0.10 to 1.00 liter per minute.

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4.3.2 Chromatographic column. Stainless steel, 2 m x 3.2 mm, containing 80/100 mesh Chromasorb 102. A secondary column of GE SF-96, 20 percent on 60/80 mesh AW Chromasorb P, stainless steel, 2 m x 3.2 mm or Porapak T, 80/100 mesh, stainless steel, 1 m x 3.2 mm is required if acetaldehyde is present. If used, a secondary column is placed after the Chromasorb 102 column. The combined columns should then be operated at 120° C.

4.3.3 Flow meters (2). Rotameter type, 0 to 100 ml/min capacity, with flow control valves.

4.3.4 Gas regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg. to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump. Leak-free. Minimum capacity 100 ml/min.

4.4 Calibration

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar bags. Sixteen-inch square size, separate bag marked for each calibration concentration.

4.4.3 Syringe. 0.5 ml, gas tight

4.4.4 Syringe. 50 ml , gas tight.

4.4.5 Flow meter. Rotameter type, 0 to 1000 ml/min range accurate to ± 1%, to meter nitrogen in preparation of standard gas mixtures.

4.4.6 Stop watch. Of known accuracy, to time gas flow in preparation of standard gas mixtures.

5. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen gas. Zero grade.

5.1.3 Oxygen gas, or Air, as required by the detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl chloride, 99.9+ percent. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysts may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen gas. Zero grade, for preparation of standard gas mixtures.

5\. Reagents. It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium gas or nitrogen gas. Zero grade, for chromatographic carrier gas.

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5.2.2 Nitrogen gas. Zero grade, for preparation of standard gas mixtures.

5.2.3 Cylinder standards (3). Gas mixture standards (50, 10, and 5 ppm vinyl chloride in nitrogen cylinders) for which the gas composition has been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that te concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.3.

5.2.3.1 Cylinder standards certification. The concentration of vinyl chloride in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) A high concentration standard (between 50 and 100 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 5 and 10 ppm) for verification of the dilution technique used.

5.2.3.2 Establishment and verification of calibration standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent: (1) verification value determined by comparison with a calibrated vinyl chloride permeation tube, (2) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1 and using 99.9+ percent vinyl chloride, or (3) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

6. Sampling.

6.1 Procedure. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve

5.2.3.2 Establishment and verification of calibration standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ±5 percent: (1) verification value determined by comparison with a calibrated vinyl chloride permeation tube, (2) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1 and using 99.9+ percent vinyl chloride, or (3) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards. All calibration standards must be renewed on a time interval consistent with the shelf life of the cylinder standards sold.

6. Sampling.

6.1 Procedure. Assemble the sample train as in Figure 106-1. Perform a bag leak check according to Section 7.4. Observe that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Sample bags must be kept out of direct sunlight. When at all possible analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection.

6.3 Sample recovery. With a piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to withdraw gas from the bag through the sample loop. Plumb the equipment so the sample gas passes from the sample valve to the leak-free pump, and then to a charcoal tube, followed by a 0-100 ml/min rotameter with flow control valve.

6.4 Analysis. Set the column temperature to 100° C, the detector temperature to 150° C, and the sample loop temperature to 70° C. When optimum hydrogen and oxygen flow rates have been determined verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, Am, by use of a disc integrator or a planimeter. Measure the peak height, Hm. Record Am, Hm and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of Hm to Am for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2)

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine and record the water vapor content of the bag.

approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, select the peak having the retention time corresponding to vinyl chloride, as determined in Section 7.2. Measure the peak area, Am, by use of a disc integrator or a planimeter. Measure the peak height, Hm. Record Am, Hm and the retention time. Repeat the injection at least two times or until two consecutive vinyl chloride peaks do not vary in area more than 5%. The average value for these two areas will be used to compute the bag concentration.

Compare the ratio of Hm to Am for the vinyl chloride sample with the same ratio for the standard peak which is closest in height. As a guideline, if these ratios differ by more than 10%, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2)

6.5 Measure the ambient temperature and barometric pressure near the bag. (Assume the relative humidity to be 100 percent.) From a water saturation vapor pressure table, determine and record the water vapor content of the bag.

7. Calibration and Standards.

7.1 Preparation of vinyl chloride standard gas mixtures. Evacuate a sixteen-inch square Tedlar bag that has passed a leak check (described in Section 7.4) and meter in 5 liters of nitrogen. While the bag is filling, use the 0.5 ml syringe to inject 250 ml of 99.9+ percent vinyl chloride through the wall of the bag. Upon withdrawing the syringe needle immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the other syringe to prepare gas mixtures having 10 and 5 ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time preparation of new gas mixtures is required. (CAUTION. Contamination may be a problem when a bag is reused if the new gas mixture standard contains a lower concentration than the previous gas mixture standard did.)

7.2 Determination of vinyl chloride retention time. This section can be performed simultaneously with Section 7.3. Establish chromatograph conditions identical with those in Section 6.3, above. Set attenuator to X 1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. With the equipment plumbing arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time record.

7.3 Preparation of chromatograph calibration curve. Make a gas mixture standard (described in Section 5.2.2 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record Cc, the concentration of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate Ac, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5 percent, then plot these points v. Cc. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10cm H_2O (2-4 in H_2O). Allow to stand for 10 minutes.

arranged identically to Section 6.3, flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures and activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined as the retention time record.

7.3 Preparation of chromatograph calibration curve. Make a gas mixture standard (described in Section 5.2.2 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with each standard gas mixture and activate the sample valve. Record Cc, the concentration of vinyl chloride injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate Ac, the peak area multiplied by the attenuator setting. Repeat until two injection areas are within 5 percent, then plot these points v. Cc. When the other concentrations have been plotted, draw a smooth curve through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.4 Bag leak checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows. To leak check, connect a water manometer and pressurize the bag to 5-10cm H_2O (2-4 in H_2O). Allow to stand for 10 minutes.

Any displacement in the water manometer indicates a leak. Also check the rigid container for leaks in this manner.

NOTE: An alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in-line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.)

8. Calculations.

8.1 Determine the sample peak area as follows:

$$A_c = A_m A_f \qquad \text{Equation 106-1.}$$

Where:

A_c= The sample peak area.

A_m= The measured peak area.

A_f= The attenuation factor.

8.2 Vinyl chloride concentrations. From the calibration curve described in Section 7.3, above, select the value of C_c that corresponds to A_c, the sample peak area. Calculate C_b as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r (1-B_{wb})} \qquad \text{Equation 106-2}$$

Where:

B_{wb} = The water vapor content of the bag sample, as analyzed.

C_b = The concentration of vinyl chloride in the bag sample in ppm.

C_c = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, ^oK.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, ^oK.

9. References

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U. S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, George, June 24, 1974.
2. "Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1.
3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract 68-02-1098. Task Order No. 7.

C_c = The concentration of vinyl chloride indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, $^{\circ}K$.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, $^{\circ}K$.

9. References

1. Brown, D. W., Loy, E. W. and Stephenson, M. H. "Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky." Region IV, U. S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, George, June 24, 1974.
2. "Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air," by G. D. Clayton and Associates, December 13, 1974. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1.
3. "Standardization of Stationary Source Emission Method for Vinyl Chloride," by Midwest Research Institute, 1976. EPA Contract 68-02-1098. Task Order No. 7.

Adopt Article 2, Subchapter 8, Chapter 1, Part III, Title 17, California Administrative Code, Sections 94100-94116, to read as follows:

Article 2. Test Methods for Determining Compliance with District Nonvehicular Emission Standards

94100. Applicability

The test methods set forth in this article shall be used to determine compliance with the nonvehicular emission standards of the districts. However, where a district board, air pollution control officer or executive officer has established a test method concerning the same subject as a test method set forth in this article, the district test method shall be used to determine compliance with the district's nonvehicular emission standards.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94101. Method 1 - Sample and Velocity Traverses.

The test procedure for determining traverse points for sample and velocity measurements is set forth in the Air Resources Board's Method 1, Sample and Velocity Traverses for Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94102. Method 2 - Velocity and Volumetric Flow Rate.

The test method for determining stack gas velocity and volumetric flow rate using a type S pitot tube is set forth in the Air Resources Board's Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube), adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94103. Method 3 - Gas Analysis.

The test method for determining carbon dioxide, oxygen, excess air and molecular weight on a dry basis in stack gases is set forth in the Air Resources Board's Method 3, Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94104. Method 4 - Moisture Content.

The test method for determining the moisture content in stack gases is set forth in the Air Resources Board's Method 4, Determination of Moisture Content in Stack Gases, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94105. Method 5 - Particulate Matter Emissions.

The test method for determining particulate matter emissions is set forth in the Air Resources Board's Method 5, Determination of Particulate Matter Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94106. Method 6 - Sulfur Dioxide.

The test method for determining sulfur dioxide emissions is set forth in the Air Resources Board's Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94107. Method 7 - Nitrogen Oxides.

The test method for determining nitrogen oxide emissions is set forth in the Air Resources Board's Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94108. Method 8 - Sulfuric Acid Mist and Sulfur Dioxide.

The test method for determining sulfuric acid mist and sulfur dioxide emissions is set forth in the Air Resources Board's Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94109. Method 10 - Carbon Monoxide.

The test method for determining carbon monoxide emissions is set forth in the Air Resources Board's Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94110. Method 11 - Hydrogen Sulfide.

The test method for determining the hydrogen sulfide content in petroleum refinery fuel gas streams is set forth in the Air Resources Board's Method 11, Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94111. Method 15 - Sulfides.

The test method for determining hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions is set forth in the Air Resources Board's Method 15, Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94112. Method 16 - Sulfur.

The test method for determining emissions of total reduced sulfur is set forth in the Air Resources Board's Method 16, Semicontinuous Determination of Sulfur Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94113. Method 17 - Particulate Matter Emissions (In-Stack).

The test method for determining particulate matter emissions using an in-stack filtration method is set forth in the Air Resources Board's Method 17, Determination of Particulate Matter Emissions from Stationary Sources (In-stack Filtration Method), adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94114. Method 100 - Continuous Sampling.

The test method for continuous gaseous emission stack sampling is set forth in the Air Resources Board's Method 100, Procedures for Continuous Gaseous Emission Stack Sampling, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94115. Method 104 - Beryllium.

The test method for determining particulate beryllium emissions is set forth in the Air Resources Board's Method 104, Determination of Beryllium Emissions from Stationary Sources, adopted June 29, 1983

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

94116. Method 106 - Vinyl Chloride.

The test method for determining vinyl chloride emissions from ethylene dichloride, vinyl chloride and polyvinyl chloride manufacturing processes is set forth in the Air Resources Board's Method 106, Determination of Vinyl Chloride Emissions from Stationary Sources, adopted June 29, 1983.

NOTE: Authority cited: Sections 39600, 39601, and 39607, Health and Safety Code. Reference: Sections 39515, 39516, 39605, 39607, and 40001, Health and Safety Code.

State of California
AIR RESOURCES BOARD

Response to Significant Environmental Issues

Item: Public Hearing to Consider Adoption of Title 17, California Administrative Code, Sections 94100-94116, Regarding Test Methods for Determining Compliance with District Nonvehicular (Stationary Source) Emission Standards

Agenda Item No.: 83-8-1

Public Hearing Date: June 29, 1983

Response Date: June 29, 1983

Issuing Authority: Air Resources Board

Comment: No comments were received identifying any significant environmental issues pertaining to this item. The staff report identified no adverse environmental effects.

Response: N/A

CERTIFIED: Harold Holmes
Board Secretary

DATE: August 26, 1983

State of California

Memorandum

To : Gordon Van Vleck
Secretary
Resources Agency

Date : December 7, 1983

Subject : Filing of Notice of Decisions of the Air Resources Board

Harold Holmes

Harold Holmes
Board Secretary
From : **Air Resources Board**

Pursuant to Title 17, Section 60007 (b), and in compliance with Air Resources Board certification under section 21080.5 of the Public Resources Code, the Air Resources Board hereby forwards for posting the attached notice of decision and response to environmental comments raised during the comment period.

ATTACHMENTS

[redacted]
83-15
83-16
83-21
83-22
83-24

RECEIVED BY
Office of the Secretary

DEC 06 1983

Resources Agency of California