United States
Environmental Protection
Agency

Air Quality Planning and Standards
Education and Outreach Group
Air Pollution Training Institute
Research Triangle Park, NC

EPA XXX/X-XX-XXX
December 2009

EPA's APTI
Course #468 Course Manual (CM)
DRAFT

Monitoring Compliance Test And Source Test Observation

Notice

This is not an official policy and standards document. The opinions and selections are those of the author and not necessarily those of the Environmental Protection Agency. Every attempt has been made to represent the present state of the art as well as subject areas still under evaluation. Any mention of products or organizations does not constitute endorsement by the United States Environmental Protection Agency (USEPA).

Usage of This Manual

The Central States Air Resource Agencies Association (CenSARA) is one of several multi-jurisdictional organizations (MJOs) operating for the U.S. Environmental Protection Agency (USEPA), through the Air Pollution Training Institute (APTI), to update more of the frequently used APTI courses. The primary objectives of the MJOs are to:

- Promote the exchange of information between the States;
- Serve as a forum to discuss regional air quality issues of common concern;
- Share resources for the common benefit of the member states; and
- Provide training services to their member air pollution control agencies.

APTI provides courses on air pollution control technology, ambient air and source monitoring, and air quality management. Historically, APTI designed courses that meet the job training needs of governmental agency personnel and others in the field of air pollution. This requires a thorough examination of both the materials for instruction and the characteristics of the student audience. Based on studies conducted by APTI of those who have participated in the various training courses, courses were developed and revised to provide training that enables every student to achieve specific course objectives. A basic goal of APTI was to provide training that will enable a student to do specific jobs in his or her home environmental agency. However, recently APTI has taken a new direction and has given money to the various MJOs, of which CenSARA is one, to update needed training course for their member states.

CenSARA meets these training needs of its member states by identifying, designing, developing and delivering needed, cost-effective, responsive, and focused educational opportunities for state and local air agency staff. Agenda and course materials are obtained from a variety of sources including EPA, colleges and universities, regional training consortia, and individual instructors. Yet, due to changes in environmental regulations, the implementation of new policies, and the advancement of technologies, agendas and course materials become out-of-date. When this happens, staffs' ability to enhance skills, knowledge and abilities are constrained, limiting their ability to excel in the dynamic field of air pollution control. So by providing up-to-date, high quality educational opportunities for staff, their chances to greatly enhance their skills, knowledge and abilities is significantly improved.

Consequently, CenSARA announced a Request for Proposals (RFP) to the environmental training community to solicit technical proposals and cost bids to review current compliance test

and observation programs within the USEPA and to **update** as necessary the content title, agenda topics, course length, instructor and student manuals, lectures involving presentation slides, classroom and homework exercises, and other handouts and materials for EPA's APTI Course 468 entitled: *"Monitoring Compliance Test and Source Test Observation."* In response to CenSARA's RFP, EnviroTech Solutions, William T. "Jerry" Winberry, 1502 Laughridge Drive, Cary, North Carolina 27511, jwinberry@mindspring.com, 919-467-2785, was awarded the contract to update EPA's APTI Course #468. Mr. Winberry is the author of this Course Manual and every attempt has been made to represent the most recent advances in sampling and analytical methodology

DISCLAIMER

This material has been developed and assembled to provide training associated with EPA's APTI Course #468 entitled: *"Monitoring Compliance Test and Source Test Observation."* It is not intended to be used for regulatory purposes, or to be a substitute for, nor interpreted as official Agency policy. Every attempt was made to reflect the technical state of art and regulatory information as of the date of this publication. This is not an official policy and standards document. The opinions and selections are those of the author and not necessarily those of the EPA. Any mention of produces or organizations does not constitute endorsement by the EPA.

U.S. Environmental Protection Agency
Air Pollution Training Institute
Course #468
Compliance Test and Source Test Observation

Course Manual (CM)

Table of Contents

U.S. Environmental Protection Agency
Air Pollution Training Institute
Course #468
Compliance Test and Source Test Observation

Chapter

1

Federal Reference Methods (FRMs)

Regulatory authority associated with the enforcement of air quality standards has its basis in the Clean Air Act and its amendments. The Clean Air Act Amendments of 1970 established the Environmental Protection Agency, which was given the mandate to set and enforce the regulations. k became the responsibility of EPA to "*protect and enhance the quality of the Nation's air resources so as to promote the public health* and *welfare and the productive capacity of its population...*" It is within this time frame that Federal Reference Methods were established to be used as regulatory methodology in determining compliance by both the Agency and the affected facility. In 197 I, the original eight FRMs were promulgated (36 FR 24877) dealing with stack gas monitoring. Since that time, FRMs have been developed to support major EPA programs dealing with New Source Performance Standards NSPS), Prevention of Significant Deteriation (PSD) and National Emission Standards for Hazardous Air Pollutants (NESHAPs), to name only a few. FRMs are methods developed in some cases for a specific source category to demonstrate compliance with an applicable standard.

As an example, FRM 16 is identified as one of the compliance methods for Subpart BB, Kraft Pulp Mills, but has also been used for monitoring total reduce sulfur (TRS) emissions from refineries, hazardous incinerators and other sources not originally intended when proposed in the regulations. Consequently, FRMs were designed with a specific need in mind for determining compliance with a pollutant emission limit. With the passage of the Act, Title III forced the Agency to look for test methodology which could quantitate many constituents at a time, thus reducing cost for an industrial source compliance program.

These methods have been proposed or promulgated in the Federal Register and codified in the Code of Federal Regulations (CFR). They carry an xx, 1xx, 2xx, or 3 xx alphanumeric designation. The xx, 1xx, and 3xx numbered methods are directly cited by specific regulations for determining compliance under 40 CFR Parts 60, 61, and 63, and may be used by sources for application as cited by the regulations and the method itself without further EPA approval.

The 2xx series methods are promulgated to facilitate incorporation in applicable State Implementation Plans. The 2xx methods, like the xx, 1xx, and 3xx series methods, include quality control and quality assurance procedures that must be met.

The abridged versions of the FRMs are not intended as regulatory documents nor are they to be used in potential enforcement issues. They are provided as a companion and reference to EPA's APTI Course #468 Student Manual (SM) to aid the user in locating the reference methods related to stack testing during the presentation of the course.

40 CFR 60 Method 1 (ABRIDGED)

Sample and Velocity Traverses for Stationary Sources

1.0 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. Traverse points are 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 m (12 in.) in diameter, or 0.071 m^2 (113 $in.^2$) cross-sectional area, or (3) the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

2.0 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. For a rectangular cross-section, an equivalent diameter (D) shall be calculated.

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

2.2 Determining the Number of Traverse Points

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 m (24 in.); (2) eight, for circular stacks with diameters between 0.30 and 0.61 m (12-24 in.); (3) nine, for rectangular stacks with equivalent diameters between 0.30 and 0.61 m (12-24 in.).

When the eight and two-diameter criterion cannot be met, the minimum number of traverse points is determined from the Figure at the end of this method. 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.

2.2.2 Velocity (Non-Particulate) Traverses

When velocity or volumetric flow rate is to be determined (but not PM), the same procedure as that for particulate traverses (Section 2.2. 1) is followed.

2.3 Cross-sectional Layout and Location of Traverse Points

2.3.1 Circular Stacks

Locate the traverse points on two perpendicular diameters. For particulate traverses, one of the diameters must be in a plane containing the greatest expected concentration variation. For stacks having diameters greater than 0.61 m (24 in.), no traverse points shall be located within 2.5 cm (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.

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. Whenever two successive traverse points are combined to form a single adjusted traverse point, treat the adjusted point as two separate traverse points, both

in the sampling (or velocity measurement) procedure, and in recording the data.

2.3.1.2 Stacks with Diameters Equal to or Less Than 0.61 m (24 in.)

Follow the procedure in Section 2.3.1.1.

2.3.2 Rectangular Stacks

Determine the number of traverse points as explained in Sections 2.1 and 2.2 of this method. 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. The situation of traverse points being too close to the stack walls is not expected to arise with rectangular stacks.

2.4 Verification of Absence of Cyclonic Flow

Cyclonic flow may exist: (1) after devices such 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 techniques for determining cyclonic flow status are provided in this section.]

An alternative procedure described in Section 2.5 may be used to determine the rotation angles.

2.5 Alternative Measurement Site Selection Procedure

This alternative applies to sources where measurement locations are less than 2 equivalent stack or duct diameters downstream or less than 1/2 duct diameter upstream from a flow disturbance. The alternative should be limited to ducts larger than 24 inches in diameter where blockage and wall effects are minimal.

2.5.1 Apparatus

2.5.1.1 Directional Probe

2.5.1.2 Any directional probe capable of measuring both the pitch and yaw angles of gas flows is acceptable. This includes differential/pressure gauges, inclined manometers, U-tube manometers, or other differential pressure gauges (e.g., magnehelic gauges) that meet the specifications described in Method 2, Section 2.2.

2.5.2 Traverse Points

Use a minimum of 40 traverse points for circular ducts and 42 points for rectangular ducts for the gas flow angle determinations.

2.5.3 Measurement Procedure

2.5.3.1 Prepare the directional probe and differential pressure gauges as recommended by the manufacturer.

2.5.3.2 Level and Zero the Manometers

Periodically check the level and zero during the traverse.

2.5.3.3 Position the probe at the appropriate locations in the gas stream, and rotate until zero deflection is indicated for the yaw angle pressure gauge. Determine and record the yaw angle. Record the pressure gauge readings for the pitch angle, and determine the pitch angle from the calibration curve. Repeat this procedure for each traverse point.

A post-test check is required.

2.5.4 Calculate the resultant angle at each traverse point, the average resultant angle, and the standard deviation.

2.5.4.1 Calculate the resultant angle at each traverse point.

2.5.4.2 Calculate the average resultant for the measurements.

2.5.4.3 Calculate the standard deviations.

2.5.5 Calibration

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

2.5.5.1 Cut two entry ports in the test section. The axis through the entry ports shall be perpendicular to each other and intersect in the centroid of the test section. The ports should be elongated slots parallel to the axis of the test section and of sufficient length to allow measurement of pitch angles while maintaining the pitot head position at the test-section centroid. To facilitate alignment of the directional probe during calibration, the test section should

be constructed of plexi-glass or some other transparent material. All calibration measurements should be made at the same point in the test section, preferably at the centroid of the test section.

2.5.5.2 To ensure that the gas flow is parallel to the central axis of the test section, follow the procedure in Section 2.4 for cyclonic flow determination.

2.5.5.3 Pitch Angle Calibration

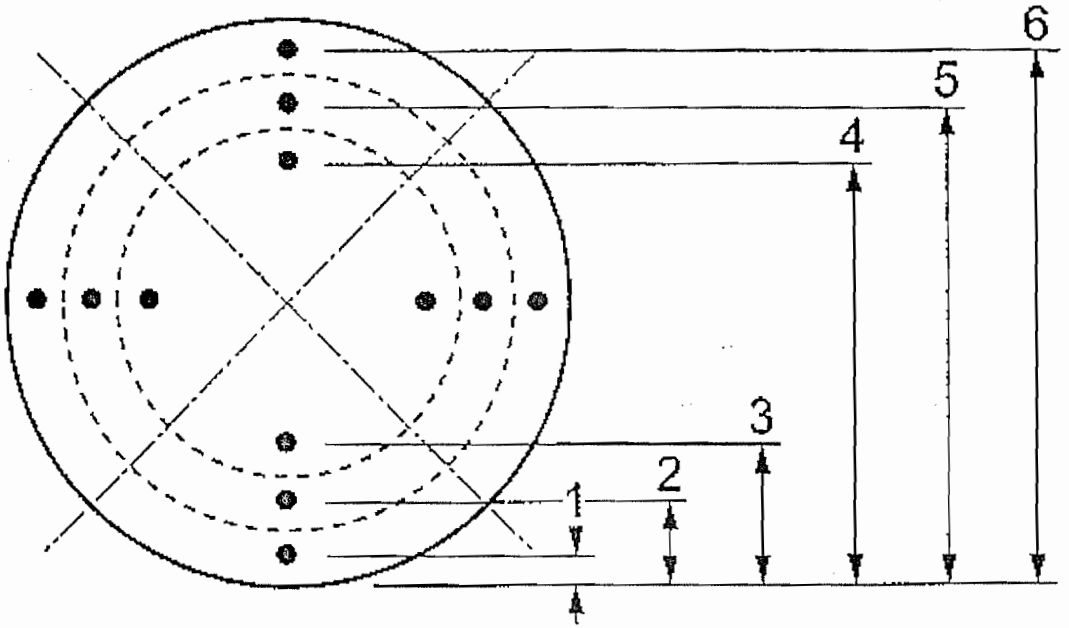
Perform a calibration traverse according to the manufacturers recommended protocol.

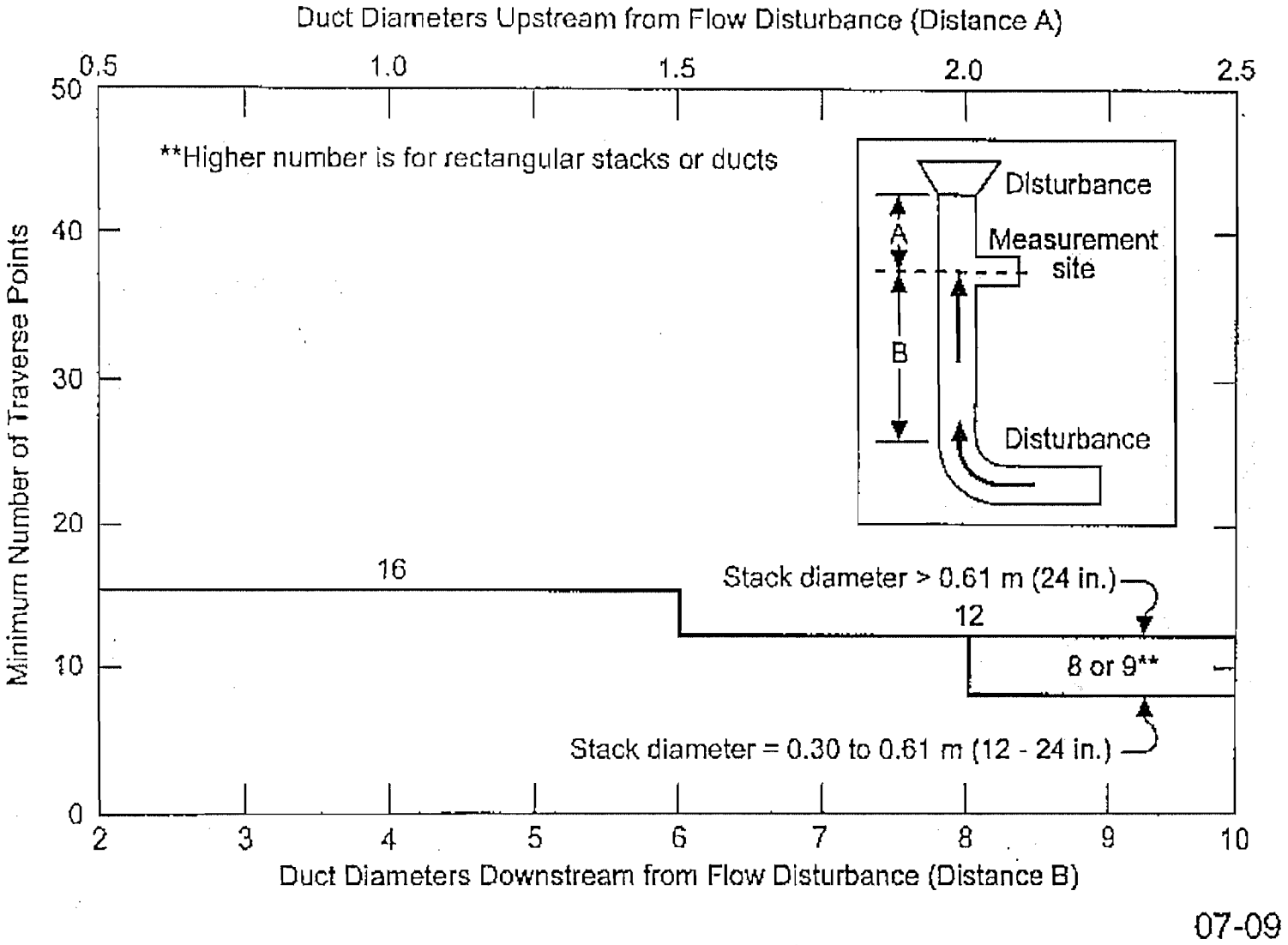
2.5.5.4 Yaw Angle Calibration

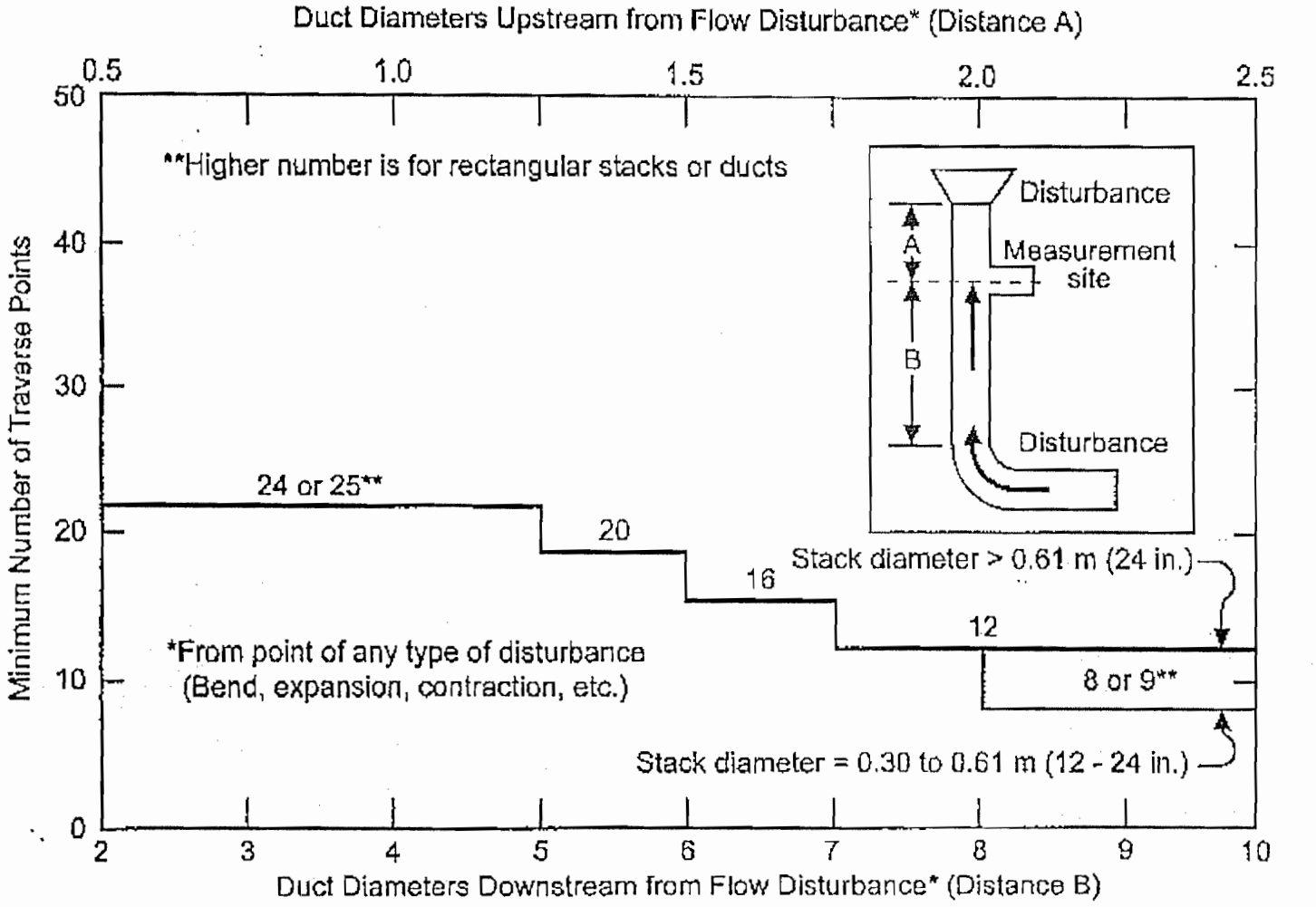
Mark the three-dimensional probe to allow the determination of the yaw position of the probe. This is usually a line extending the length of the probe and aligned with the impact opening.

Pt. 60, App. Meth. 1

Traverse Point	Distance, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6




Duct Diameters Upstream from Flow Disturbance (Distance A)
0.5
1.0
1.5
2.0
2.5
50
40
30
20
10
0
**Higher number is for rectangular stacks or ducts
Disturbance
A
Measurement site
B
Disturbance
16
Stack diameter > 0.61 m (24 in.)
12
8 or 9**
Stack diameter = 0.30 to 0.61 m (12 - 24 in.)
Minimum Number of Traverse Points
2
3
4
5
6
7
8
9
10
Duct Diameters Downstream from Flow Disturbance (Distance B)
07-09


Duct Diameters Upstream from Flow Disturbance* (Distance A)
0.5
1.0
1.5
2.0
2.5
50
40
30
20
10
0
**Higher number is for rectangular stacks or ducts
Disturbance
A
Measurement site
B
Disturbance
24 or 25**
20
16
12
8 or 9**
Stack diameter > 0.61 m (24 in.)
Stack diameter = 0.30 to 0.61 m (12 - 24 in.)
*From point of any type of disturbance
(Bend, expansion, contraction, etc.)
Minimum Number of Traverse Points
2
3
4
5
6
7
8
9
10
Duct Diameters Downstream from Flow Disturbance* (Distance B)

07-08

Table 1-2. Location of Traverse Points in Circular Stacks

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

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

40 CFR 60 Method 2 (ABRIDGED)

Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube)

1.0 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 that 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.

2.0 Apparatus

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

2.1 Type-S Pitot Tube

The Type-S Pitot Tube shall be made of metal tubing (e.g., stainless steel). It is recommended that the external tubing diameter be between 0.48 and 0.95 cm (3/16 and 3/8 in.).

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, which 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 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.

2.2 Differential Pressure Gauge

An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10-inch (water column) inclined vertical manometer, having 0.01-inch H_2O divisions on the 0 to 1-inch inclined scale, and 0.1-inch H_2O divisions on the 1 to 10-inch 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.

If the manometer reading 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.

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.

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.

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.

2.6 Gas Density Determination Equipment

Method 3 equipment, if needed (see Section 3.6), to determine the stack gas dry molecular weight, and Reference Method 4

or Method 5 equipment for moisture content determination; other methods may be used subject to approval of the Administrator.

2.7 Calibration Pitot Tube

When calibration of the Type-S pitot tube is necessary (see Section 4), a standard pitot tube is used as a reference. The standard pitot tube shall, preferably, have a known coefficient. Alternatively, a standard pitot tube designed according to the criteria given in 2.7.1 through 2.7.5 may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 to 1.01.

2.7.1 Hemispherical, 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.

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, the calibration differential pressure gauge shall be readable to the nearest 0.13 mm H_2O (0.005 in. H_2O).

3.0 Procedure

3.1 Leak Check Pitot Tube

Set up the apparatus as shown in the Figure at the end of this method. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to damper Δp fluctuations. It is recommended, but not required, that a pretest leak check be conducted.

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.

3.3 Measurement

Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of Δp values encountered (see Section 2.2). Conduct a post-test leak check (mandatory), as described in Section 3.1 above, to validate the traverse run.

3.4 Measurement of Static Pressure

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

3.5 Measurement of Atmospheric Pressure

Determine the atmospheric pressure.

3.6 Measurement of Stack Gas Dry Molecular Weight

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.

3.7 Measurement of Moisture

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

3.8 Measurement of Cross-Sectional Area

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.

4.0 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 specifications. The pitot tube shall not be used if it fails to meet alignment specifications.

After verifying the face opening alignment, measure and record the dimensions of the pitot tube.

If D_t, P_A and P_B are outside the specified limits, the pitot tube must be calibrated.

4.1.1 Type-S Pitot Tube Assemblies

The presence of other sampling components can sometimes affect the baseline value of the Type-S pitot tube coefficient; therefore, an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly.

NOTE: Do not use any Type-S pitot tube assembly that is constructed so that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle.

4.2 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.

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

4.2.2 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 calculation to determine the number of duct diameters.

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

NOTE: The eight- and two-diameter criteria are not absolute.

4.2.3 Calibration Procedure

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

4.2.3.1 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.

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

4.2.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point and align the tube so that its tip is pointed directly into the flow.

4.2.3.4 Read Δp_{std} and record its value in a data table. Remove the standard pitot tube from the duct and disconnect it from the manometer. Seal the standard entry port.

4.2.3.5 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 the standard pitot tube was and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.2.3.6 Read Δp_{std} and enter its value in the data table. Remove the Type-S pitot tube from the duct and disconnect it from the manometer.

4.2.3.7 Repeat steps above until three pairs of Δp readings have been obtained.

4.2.3.8 Repeat steps above for the B-side of the Type-S pitot tube.

4.2.3.9 Perform calculations as described below.

4.2.4 Calculations

4.2.4.1 For each of the six pairs of Δp readings (i.e., three from side A and three from side B) obtained above, calculate the value of the Type-S pitot tube coefficient.

4.2.4.2 Calculate C_p (side A), the mean A-side coefficient, and C_p (side B), the mean B-side coefficient; calculate the difference between these two average values.

4.2.4.3 Calculate the deviation of each of the three, A-side values of C_p from C_p (side A) and the deviation of each of the three, B-side values of C_p from C_p (side B).

4.2.4.4 Calculate, the average deviation from the mean, for both the A and B sides of the pitot tube.

4.2.4.5 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 C_p (side A) and C_p (side B) is 0.01 or less.

4.2.5 Special considerations

4.2.5.1 Selection of Calibration Point

4.2.5.1.1 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 above.

4.2.5.1.2 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 above.

4.2.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values.

4.2.5.1.4 For the 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 specifications), the value of C_p 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.

4.2.5.2 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 that will face the flow).

4.2.6 Field Use and Re-calibration

4.2.6.1 Field Use

4.2.6.1.1 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.

4.2.6.1.2 When a probe assembly is used to sample a small duct (12 to 36 inches 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. Conventional pitot sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches.

4.2.6.2 Re-calibration

4.2.6.2.1 Isolated Pitot Tubes

After each field use, the pitot tube shall be carefully re-examined in top, side, and end views. If the pitot face openings are still aligned within the specifications, 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, the damage shall either be repaired to restore proper alignment of the face openings or the tube shall be discarded.

4.2.6.2.2 Pitot Tube Assemblies

After each field use, check the face opening alignment of the pitot tube; also, re-measure the inter-component spacings of the assembly. If the inter-component 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, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the inter-component spacings have changed, restore the original spacing or re-calibrate the assembly.

4.3 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.

4.4 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.

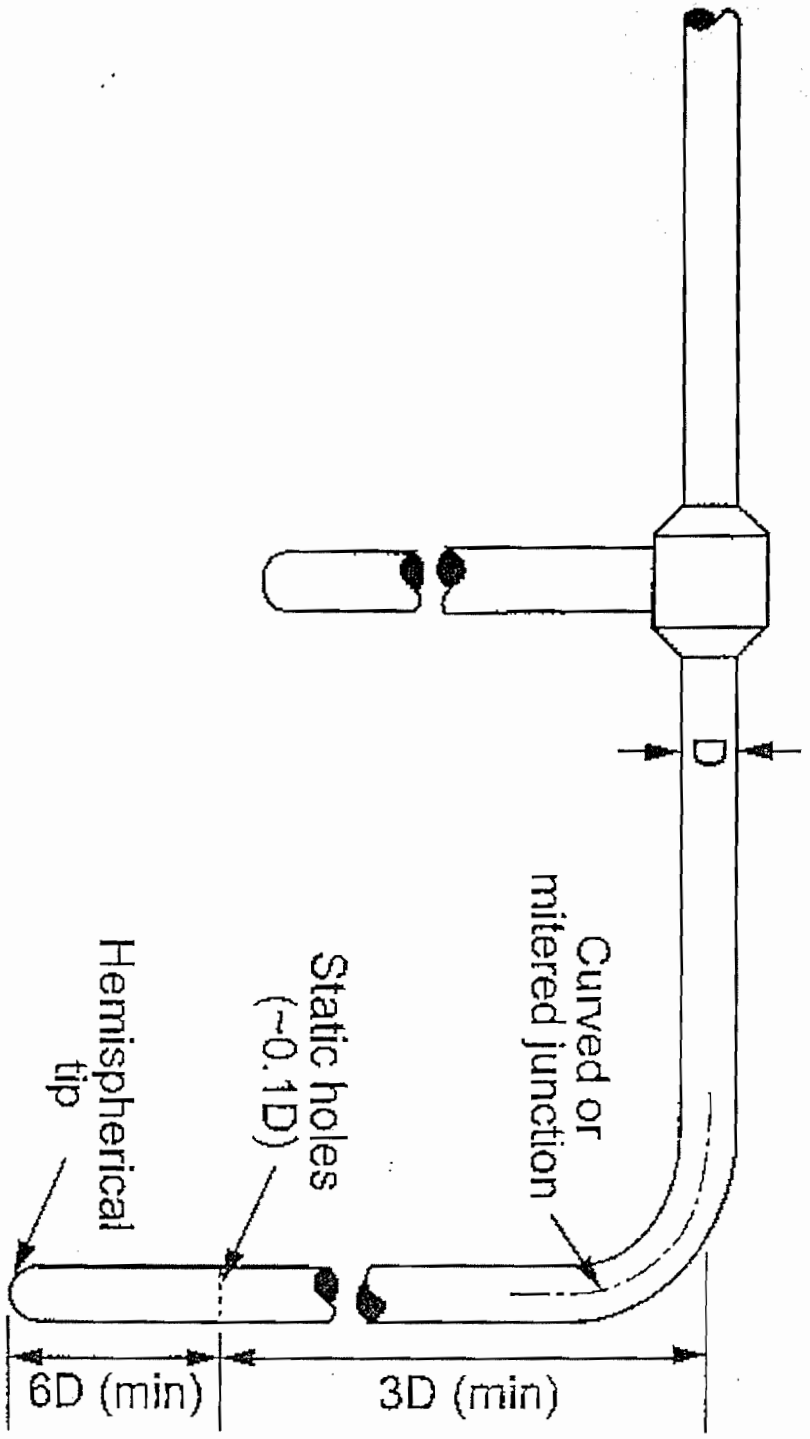
If, during calibration, the absolute temperatures measured with the gauge being calibrated and the reference gauge agree within 1.5 percent, the temperature data taken in the field shall be considered valid.

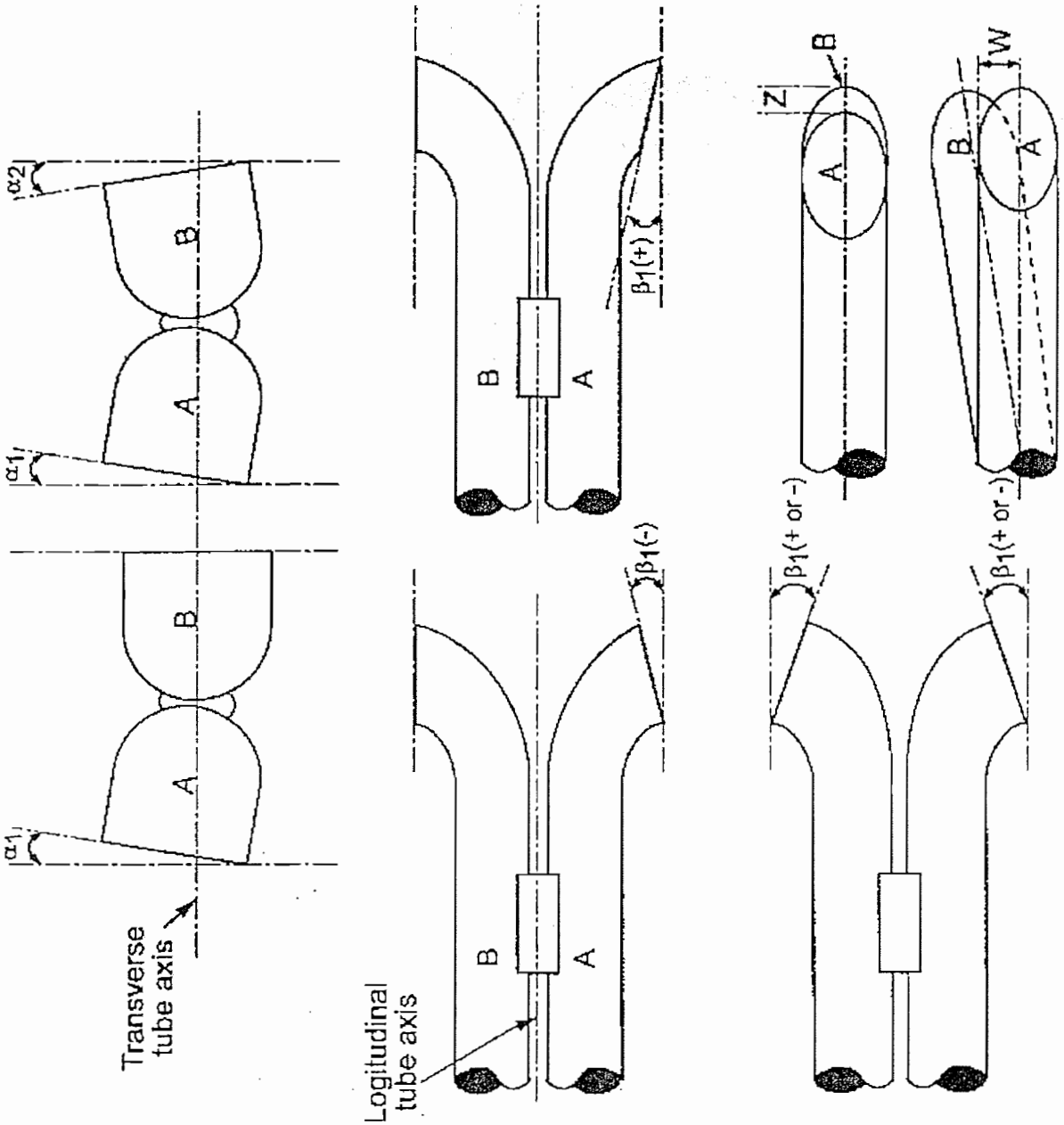
4.5 Barometer

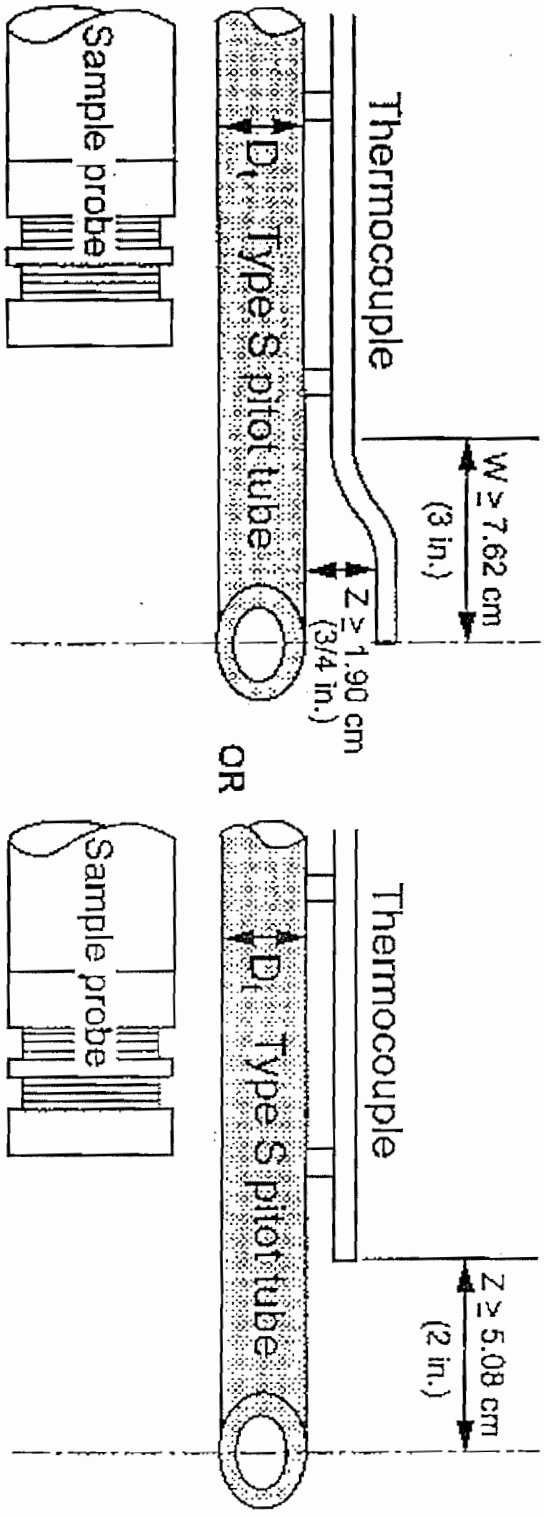
Calibrate the barometer used against a mercury barometer.

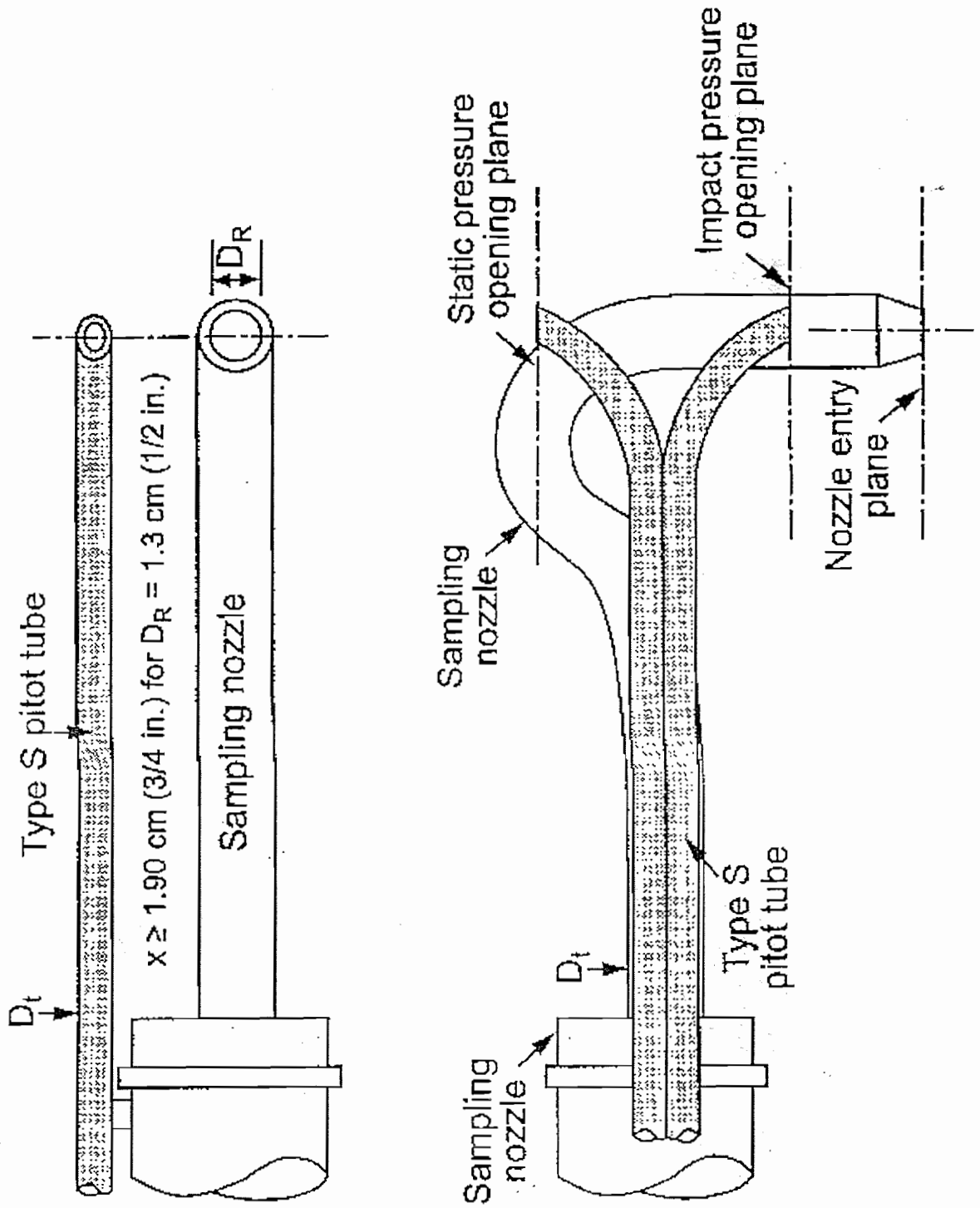
5.0 Calculations

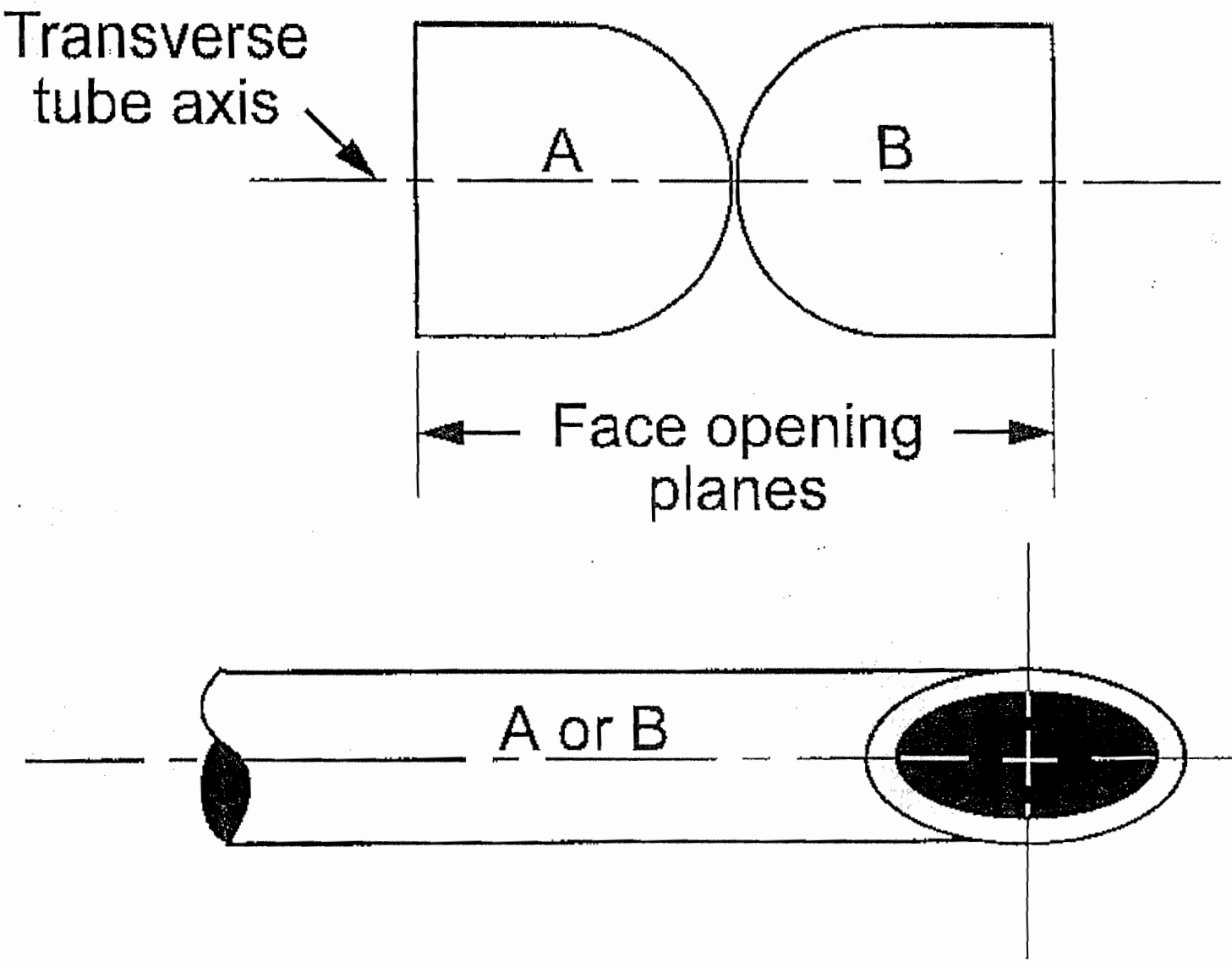
Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

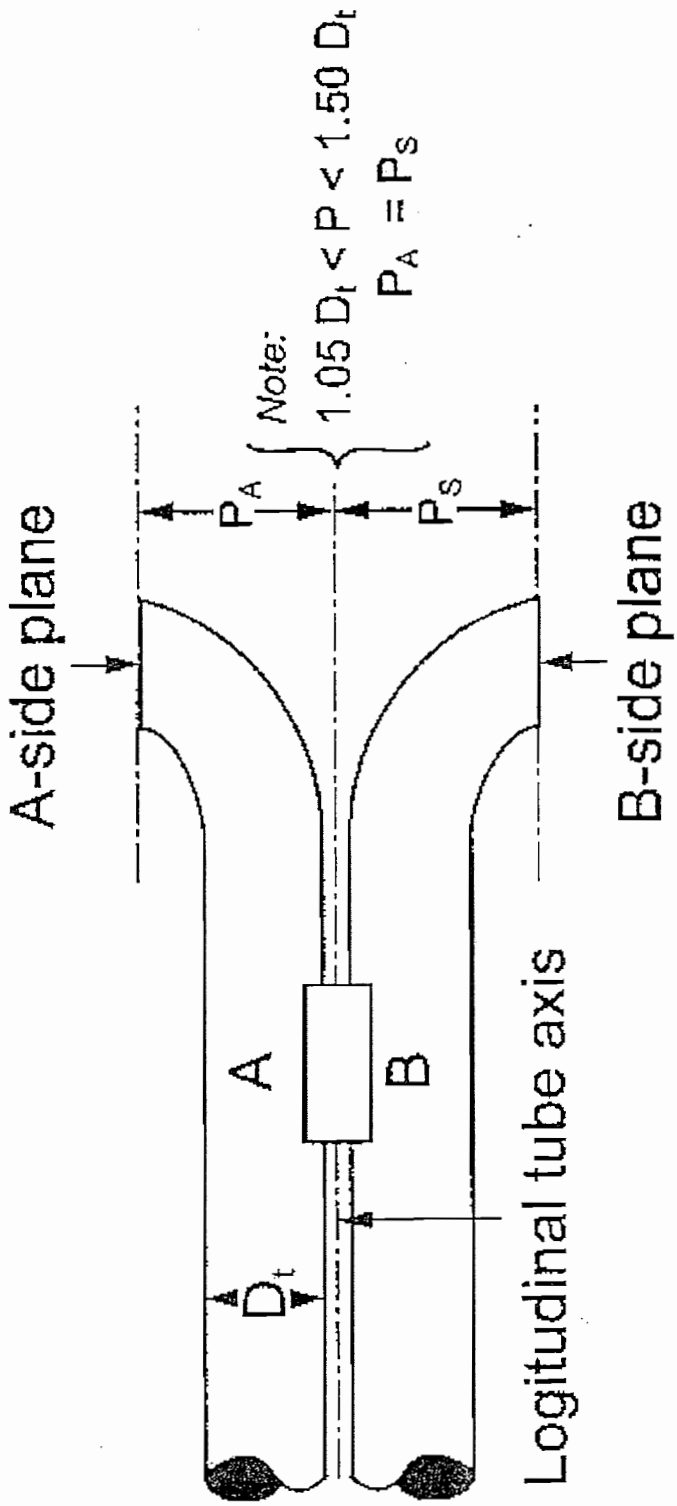

D
Curved or
mitered junction
Static holes
(~0.1D)
Hemispherical
tip
6D (min)
3D (min)

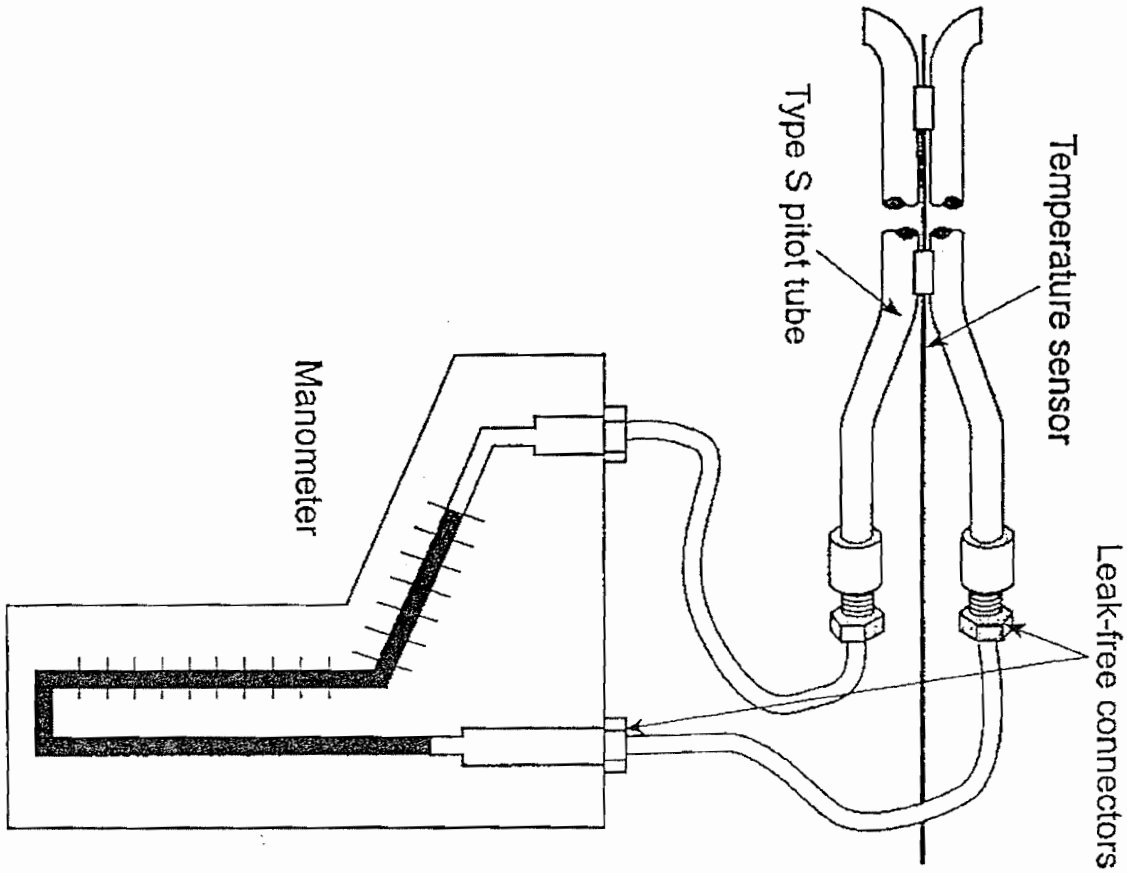

α2
B
A
α1
B
A
α1
Transverse tube axis
B
A
β1(+)
B
A
β1(-)
Logitudinal tube axis
Z
B
A
β1(+ or -)
W
B
A
β1(+ or -)


Sample probe
Thermocouple
D, Type S pitot tube
W ≥ 7.62 cm
(3 in.)
Z ≥ 1.90 cm
(3/4 in.)
OR
Sample probe
Thermocouple
D, Type S pitot tube
Z ≥ 5.08 cm
(2 in.)


Type S pitot tube
D_t
$x \geq 1.90$ cm (3/4 in.) for $D_R = 1.3$ cm (1/2 in.)
Sampling nozzle
D_R
Static pressure opening plane
Impact pressure opening plane
Sampling nozzle
Nozzle entry plane
D_t
Type S pitot tube
Sampling nozzle


Transverse
tube axis
A
B
Face opening
planes
A or B


A-side plane
B-side plane
Logitudinal tube axis
A
B
D_t
P_A
P_S
Note:
1.05 D_t < P < 1.50 D_t
$P_A = P_S$


Type S pitot tube
Temperature sensor
Manometer
Leak-free connectors

40 CFR 60 Method 3 (ABRIDGED)

Gas Analysis for the Determination of Dry Molecular Weight

1.0 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) multipoint, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO_2), percent oxygen (O_2), and if necessary, for percent carbon monoxide (CO). For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used.

1.2 Applicability

1.2.1 Determination

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

1.2.2 Modifications

Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) a multipoint sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight; and (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil.

2.0 Apparatus

As an alternative to the sampling apparatus and systems described herein, other sampling systems (e.g., liquid displacement) may be used. Use of such systems is subject to the approval of the Administrator.

2.1 Grab Sampling

2.1.1 Probe

Stainless steel or borosilicate glass tubing equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose).

2.1.2 Pump

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

2.2 Integrated Sampling

2.2.1 Probe

Same as in Section 2.1.1.

2.2.2 Condenser

An air-cooled or water-cooled condenser.

2.2.3 Valve

A needle valve, to adjust sample gas flow rate.

2.2.4 Pump

A leak-free, diaphragm-type pump, or equivalent, to transport sample gas to the flexible bag.

2.2.5 Rate Meter

A rotameter, or equivalent rate meter, capable of measuring flow rate to within 2 percent of the selected flow rate. A flow rate range of 500 to 1000 cc/min is suggested.

2.2.6 Flexible Bag

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

2.2.7 Pressure Gauge

A water-filled U-tube manometer, or equivalent.

2.2.8 Vacuum Gauge

A mercury manometer, or equivalent.

2.3 Analysis

An Orsat or Fyrite-type combustion gas analyzer.

3.0 Single Point, Grab Sampling and Analytical Procedure

3.1 Sampling Point

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).

3.2 Set-up Equipment

Set up the equipment as shown in the Figure at the end of this method.

3.3 Sampling

Place the probe in the stack, with the tip of the probe positioned at the sampling point. Purge the sampling line long enough to allow at least five exchanges. Draw a sample into the analyzer and immediately analyze it for percent CO_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 7.2.

3.4 Repeat Sampling

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

4.0 Single Point, Integrated Sampling and Analytical Procedure

4.1 Sampling Point

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

4.2 Leak Check

Leak check (optional) the flexible bag as described in Section 2.2.6.

4.3 Sampling

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.

4.4 Analysis

4.5 Repeat Analysis

5.0 Multipoint, Integrated Sampling and Analytical Procedure

5.1 General

Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of 12 traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Administrator.

5.2 Exceptions

Follow the procedures outlined in Sections 4.2 through 4.5.

6.0 Leak Check Procedure for Orsat Analyzer

The Orsat analyzer should be thoroughly leak checked on site before the flue gas sample is introduced into it.

6.1 Operation

Bring the liquid level in each pipette up to the reference mark on the capillary tubing, and then close the pipette stopcock. Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette, and then close the manifold stopcock. Record the meniscus position. Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

6.2 Criteria

For the Orsat analyzer to pass the leak check, two conditions must be met: (1) the liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval; and (2) the meniscus in the burette must not change by more than 0.2 mL during this 4-minute interval.

6.3 Failure

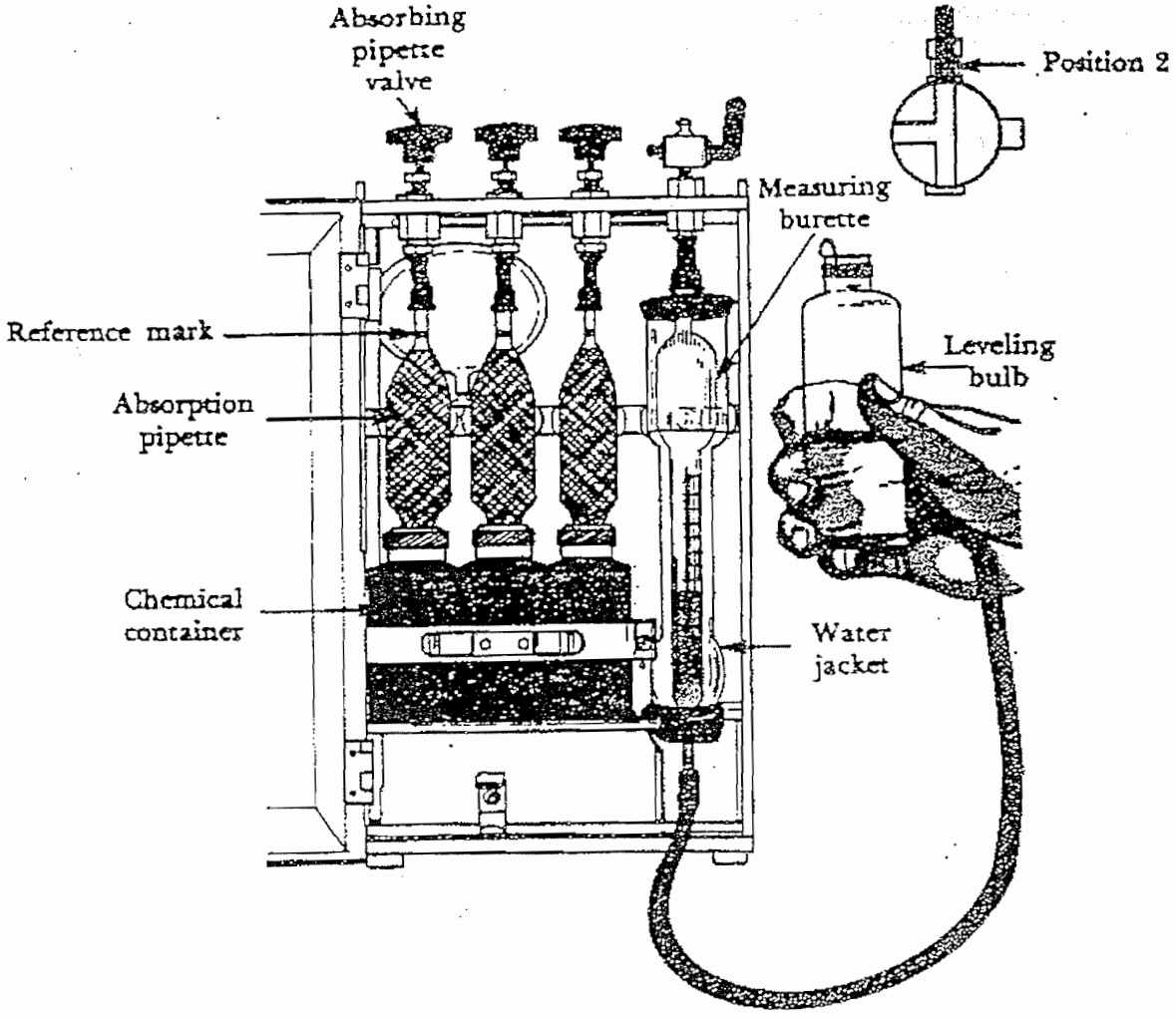
If the analyzer fails the leak check procedure, check all the rubber connections and stopcocks to determine whether they might be the cause of the leak. Disassemble, clean, and regrease leaking stopcocks. Replace leaking rubber connections. After the analyzer is reassembled, repeat the leak check procedure.

7.0 Calculations

7.1 Nomenclature

7.2 Dry Molecular Weight

Calculate the dry molecular weight of the stack gas.


Absorbing pipette valve
Position 2
Measuring burette
Reference mark
Leveling bulb
Absorption pipette
Chemical container
Water jacket

40 CFR 60 Method 3A (ABRIDGED)

Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)

1.0 Principle and Applicability

1.1 Principle

A sample is continuously extracted from the effluent stream and a portion of the sample stream is conveyed to an instrumental analyzer(s) for determination of oxygen (O_2) and carbon dioxide (CO_2) concentration(s).

1.2 Applicability

This method is applicable to the determination of O_2 and CO_2 concentrations in emissions from stationary sources.

2.0 Range and Sensitivity

Same as Method 6C, Sections 2.1 and 2.2, except the span of the monitoring system shall be such that the average O_2 and CO_2 concentration is not less than 20 percent of the span.

3.0 Definitions

3.1 Measurement System

The measurement system consists of the same major subsystems as defined in Method 6C.

3.2 Other Systems

Same as Method 6C.

3.3 Interference Response

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

4.0 Measurement System Performance Specifications

Same as Method 6C.

5.0 Apparatus and Reagents

5.1 Measurement System

Any measurement system for O_2 or CO_2 that meets the specifications of this method. A schematic of an acceptable measurement system is shown in the Figure at the end of Method 6C.

5.1.1 Sample Probe

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

5.1.2 Sample Line

Tubing, to transport the sample gas from the probe to the moisture removal system.

5.1.3 Other Equipment

Same as Method 6C, except that the requirements to use stainless steel, Teflon®, and non-reactive glass filters do not apply.

5.1.4 Gas Analyzer

An analyzer to continuously determine the O_2 or CO_2 concentration in the sample gas stream.

5.2 Calibration Gases

The calibration gases for CO_2 analyzers shall be CO_2 in nitrogen (N_2), or CO_2 in air. Alternatively, CO_2 /SO_2, O_2/SO_2, or O_2/CO_2/SO_2 gas mixtures in N_2 may be used.

6.0 Measurement System Performance Test Procedures

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

6.1 Calibration Concentration Verification

Follow Method 6C, except if calibration gas analysis is required, use Method 3.

6.2 Interference Response

Conduct an interference response test of the analyzer prior to its initial use in the field. Conduct the interference response in accordance with Section 5.4 of Method 20.

6.3 Other Procedures

Follow Method 6C.

7.0 Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points

Same criteria that are applicable to tests performed using Method 3.

7.2 Sample Collection

Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check.

7.3 Zero and Calibration Drift Test

Follow Method 6C.

8.0 Quality Control Procedures

The following quality control procedures are recommended.

8.1 Validate Results

If both O_2 and CO_2 are measured using Method 3A, the procedures described in Section 4.4 of Method 3 should be followed to validate the O_2 and CO_2 measurement results.

If only O_2 is measured using Method 3A, measurements of the sample stream CO_2 concentration should be obtained at the sample by pass vent discharge using an Orsat or Fyrite analyzer.

If only CO_2 is measured using Method 3A, concurrent measurements of the sample stream CO_2 concentration should be obtained using an Orsat or Fyrite analyzer as described in Section 8.2.

9.0 Emission Calculation

For all CO_2 analyzers, and for O_2 analyzers that can be calibrated with zero gas, follow Method 6C, except express all concentrations as percent, rather than ppm.

40 CFR 60 Method 4 (ABRIDGED)

Determination of Moisture Content in Stack Gases

1.0 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.

NOTE: This 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.

2.0 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 the Figure at the end of this method. 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 or heated out-stack to remove particulate matter.

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 cm (1/2 in.) I.D. 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.

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. A thermometer, capable of measuring temperature to within 1°C (2°F), shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system may be used (subject to the approval of the Administrator) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 mL or 1 g.

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 volume to within 2 percent, and related equipment as shown in the Figure at the end of this method.

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. The barometric reading may be obtained from a nearby National Weather Service station.

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.

2.2 Procedure

The following procedure is written for a condenser system incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 Traverse Points

Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.); a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.); and a minimum of 12 traverse points shall be used in all other cases. The traverse points shall be located according to Method 1.

2.2.2 Selection of Sampling Time

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 Sampling Train

Set up the sampling train as shown in the Figure at the end of this method. 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 and allow time for the temperatures to stabilize. Place crushed ice in the ice bath container.

It is recommended, but not required, that a leak check be done.

2.2.4 Maintaining Samping Rate

During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted.

2.2.5 Positioning the Probe

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 Sample Recovery

After collecting the sample, disconnect the probe from the filter holder (or from the first impinger) and conduct a leak check (mandatory). 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. Measure the volume of the moisture condensed to the nearest milliliter. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g.

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

2.3 Calculations

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

2.3.1 Nomenclature

2.3.2 Volume of Water Vapor Condensed

2.3.3 Volume of Water Vapor Collected in Silica Gel

2.3.4 Sample GasVolume

NOTE: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of V in Method 5.

2.3.5 Moisture Content

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

2.3.6 Verification of Constant Sampling Rate

For each time increment, determine the delta V_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3.0 Approximation Method

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

3.1 Apparatus

3.1.1 Probe

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

3.1.2 Impingers

Two 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 L/min (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 Charging Sampling Train

Place exactly 5 mL distilled water in each impinger.

Leak check the sampling train.

3.2.2 Sample Train Operation

Connect the probe, insert it into the stack, and sample at a constant rate of 2 L/min (0.071 cfm). Continue sampling until the dry gas meter registers about 30 L (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.

3.2.3 Sample Train Recovery

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 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 equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature

3.3.2 Volume of Water Vapor Collected

3.3.3 Gas Volume

3.3.4 Approximate Moisture Content

4.0 Calibration

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. For the approximation method, use the procedures outlined in Section 5.1.1 of Method 6 to calibrate the metering system, and the procedure of Method 5, Section 5.7 to calibrate the barometer.

468-R-5.doc

40 CFR 60 Method 5 (ABRIDGED)

Determination of Particulate Emissions from Stationary Sources

1.0 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).

1.2 Applicability

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

2.0 Apparatus

2.1 Sampling Train

A schematic of the sampling train used in this method is shown in the Figure at the end of this method.

2.1.1 Probe Nozzle

Stainless steel (316) or glass with sharp, tapered leading edge.

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]. 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). Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825®, or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners.

2.1.3 Pitot Tube

Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The Type-S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2.

2.1.4 Differential Pressure Gauge

Inclined manometer or equivalent devices (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.

2.1.5 Filter Holder

Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. 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).

2.1.7 Condenser

The following system shall be used to determine the stack gas moisture content: four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third and fourth impingers shall be of the Greenberg-Smith design, modified by replacing the tip with 1.3 cm (1 /2 in.) I.D. glass tube extending to about 1-3 cm (1 /2 in.) from the bottom of the flask. The second impinger shall be of the Greenberg-Smith design with the standard tip. 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°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

2.1.8 Metering System.

Vacuum gauge, leak-free pump, thermometer 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 the Figure at the end of this method.

2.1.9 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm of Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station.

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.

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.

2.2.2 Wash Bottles

Two glass wash bottles.

2.2.3 Glass Sample Storage Containers

Chemically resistant, borosilicate glass bottles, for acetone washes, 500 mL and 1000 mL. Screw cap liners shall be rubber-backed Teflon® or shall be constructed so as to be leak-free and resistant to chemical attack by acetone.

2.2.4 Petri Dishes

Glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder, and/or Balance

To measure condensed water to within 1 mL or 1 g.

2.2.6 Plastic Storage Containers

Air-tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman

2.2.8 Funnel

Glass or polyethylene.

2.3 Analysis

3.0 Reagents

3.1 Sampling

3.1.1 Filters

Glass fiber filters.

3.1.2 Silica Gel

Indicating type, 6 to 16-mesh.

3.1.3 Water

When analysis of the material caught in the impingers is required, deionized distilled water shall be used.

3.1.4 Crushed Ice

3.1.5 Stopcock Grease

Acetone, insoluble, heat-stable silicone grease.

3.2 Sample Recovery

Acetone (reagent grade), <0.001 percent residue, in glass bottles is required.

3.3 Analysis

Two reagents are required for the analysis:

3.3.1 Acetone

3.3.2 Desiccant

4.0 Procedure

4.1 Sampling

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

4.1.1 Pretest Preparation

It is suggested that sampling equipment be maintained according to the procedure described in APTD-0576.

Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, for each container.

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. Record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively,

(unless otherwise specified by the Administrator), the filters may be oven dried at 105°C (220°F) for 2 to 3 hours, desiccated for 2 hours, and weighed.

4.1.2 Preliminary Determinations

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

Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates.

Select a suitable probe liner and probe length. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the 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 and (2) the sample volume taken will exceed the required minimum total gas sample volume.

4.1.3 Preparation of Collection Train

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

Place 100 mL of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel can be used, but care should be taken to ensure 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.

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 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® O-ring when stack temperatures are less than 260°C (500°F) and an asbestos string gasket when temperatures are higher. 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 shown in the Figure at the end of this method.

Place crushed ice around the impingers.

4.1.4 Leak Check Procedures

4.1.4.1 Pretest Leak Check

A pretest leak check is recommended, but not required.

4.1.4.2 Leak Checks During Sampling Run

If, during the sampling run, a component (e.g., filter assembly or impinger) change become 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.

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.

4.1.5 Particulate Train Operation

During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic and a temperature around the filter of 120 ± 14°C (248 ± 25°F).

For each run, record the data required on a data sheet.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material.

Immediately start the pump and adjust the flow to isokinetic conditions.

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.

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

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator.

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

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

A single train shall be used for the entire sampling 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.

At the end of the sampling 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.

4.2 Sample Recovery

Proper cleanup procedures begin as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

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.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. 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. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet.

Transfer the probe and filter/impinger assembly to the cleanup area.

Container No.1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold.

Container No. 2. See that dust on the outside of the probe or other exterior surfaces does not get into the sample. Quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container.

Perform the acetone rinses.

Follow the acetone rinse with a probe brush. Rinse the brush with acetone, and quantitatively collect these washings in the sample container.

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.

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. Record the volume or weight of liquid present.

4.3 Analysis

Record the data required on a sheet.

4.4 Quality Control Procedures

These procedures are optional for the tester.

4.4.1 Meter Orifice Check

Using the calibration data obtained during the calibration procedure described in Section 5.3, determine the $\Delta H_@$ for the metering system orifice.

Calculate a dry gas meter calibration check value, Y_c.

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

$$0.97\,Y < Y < 1.03\,Y$$

4.4.2 Calibrated Critical Orifice

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

5.0 Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle

Probe nozzles shall be calibrated before their initial use in the field.

5.2 Pitot Tube

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

5.3 Metering System

5.3.1 Calibration Prior to Use

Before its initial use in the field, the metering system shall be calibrated.

5.3.2 Calibration After Use

After each field use, the calibration of the metering system shall be checked by performing three calibration runs.

5.3.3 Acceptable Variations in Calibration

If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or use lower value coefficient.

5.4 Probe Heater Calibrations

The probe heating system shall be calibrated before its initial use in the field.

5.5 Temperature Gauges

Use the procedure found in Method 2 to calibrate in-stack temperature gauges.

5.6 Leak Check of Metering System

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.

5.7 Barometer

Calibrate against a mercury barometer.

6.0 Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data.

6.1 Nomenclature

6.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

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).

NOTE: Leak rate equations can be used as written unless the leakage rate observed during any of the mandatory leak checks exceeds L_a. If L_p or L_i exceeds L_a, the equation must be modified by using Case I or Case II equations in Method 5.

6.4 Volume of Water Vapor

6.5 Moisture Content

6.6 Acetone Blank Concentration

6.7 Acetone Wash Blank

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.

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

6.10 Conversion Factors

6.11 Isokinetic Variation

6.11.1 Calculation from Raw Data

6.11.2 Calculation from Intermediate Values

6.12 Acceptable Results

If 90 percent < I < 110 percent, the results are acceptable.

6.13 Stack Gas Velocity and Volumetric Flow Rate

Calculate the average stack gas velocity and volumetric flow rate.

7.0 Alternative Procedures

7.1 Dry Gas Meter as a Calibration Standard

A dry gas meter may be used as a calibration standard for volumetric measurements.

7.1.1 Standard Dry Gas Meter Calibration

7.1.1.1 The dry gas meter to be calibrated and used as a secondary reference meter should be of a high quality and have an appropriately sized capacity.

7.1.1.2 Set up the components as shown in the Figure at the end of this method.

7.1.1.3 Collect the data.

7.1.1.4 Calculate flow rate, Q, for each run.

7.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values.

7.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the dry gas meter.

7.1.2 Standard Dry Gas Meter Recalibration

7.1.2.1 Recalibrate the standard dry gas meter against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first.

7.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made.

7.2 Critical Orifices as Calibration Standards

Critical orifices may be used as calibration standards in place of the wet test meter specified in Section 5.3.

7.2.1 Selection of Critical Orifices

7.2.1.1 The procedure that follows describes the uses of hypodermic needles, which have been found suitable for use as critical orifices.

7.2.1.2 Adapting needles to a Method 5 type sampling train.

7.2.2 Critical Orifice Calibration

The procedure described in this section uses the Method 5 meter box configuration with a dry gas meter (DGM) as described in Section 2.1.8 to calibrate the critical orifices.

7.2.2.1 Calibration of Meter Box

The critical orifices may be calibrated in the same configuration as they will be used.

7.2.2.1.1 Before calibrating the meter box, leak check the system.

7.2.2.1.2 Check for leakages in that portion of the sampling train between the pump and the orifice meter.

7.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box

according to the procedure given in Section 5.3.

7.2.2.2 Calibration of Critical Orifices

7.2.2.2.1 Allow a warm-up time of 15 minutes.

7.2.2.2.2 Leak check the system. The leakage rate shall be zero.

7.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum.

7.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section 2.1.9.

7.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum.

7.2.2.2.6 Calculate K'

7.2.3 Use the Critical Orifices as Calibration Standards

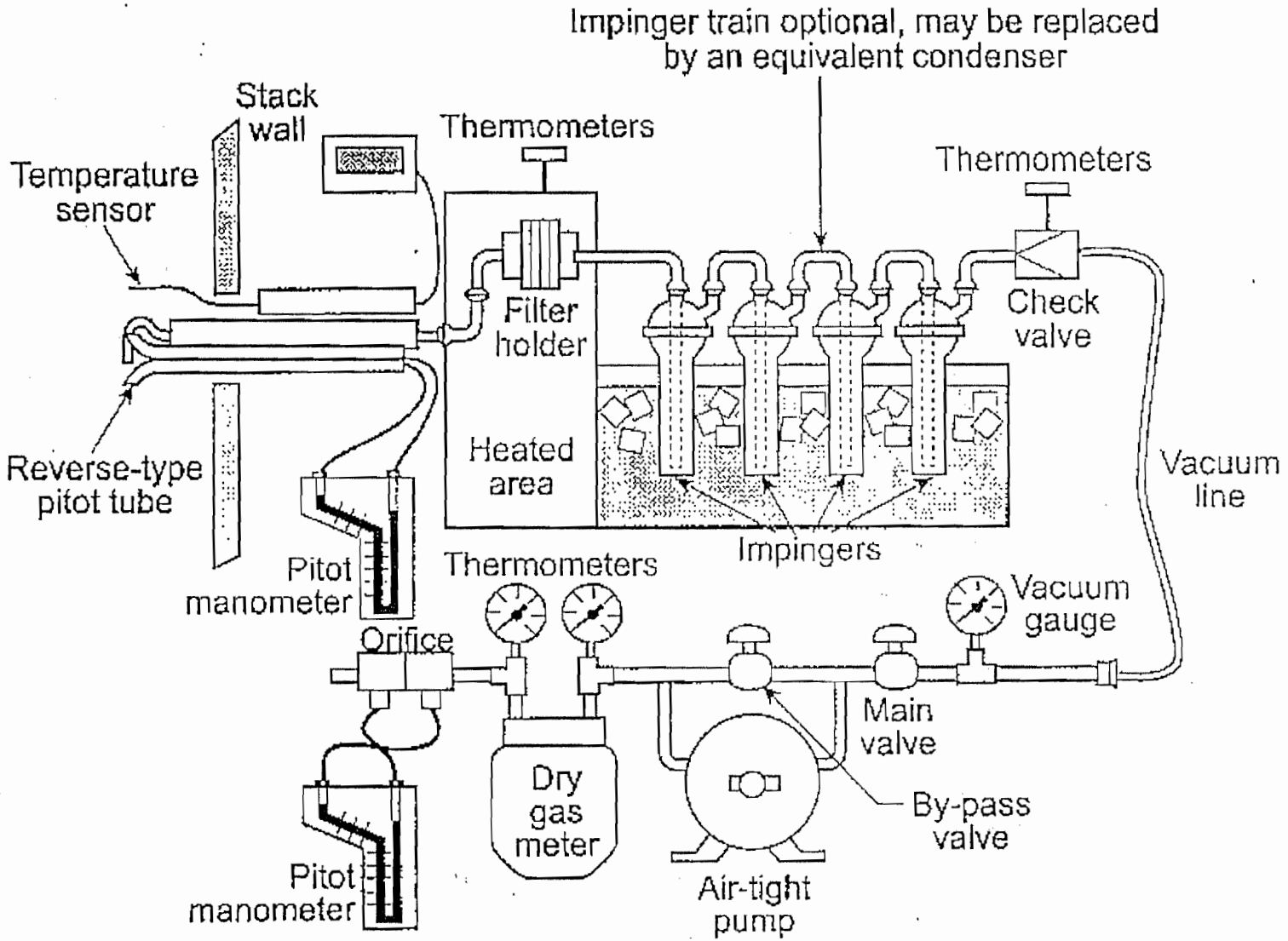
7.2.3.1 Record the barometric pressure.

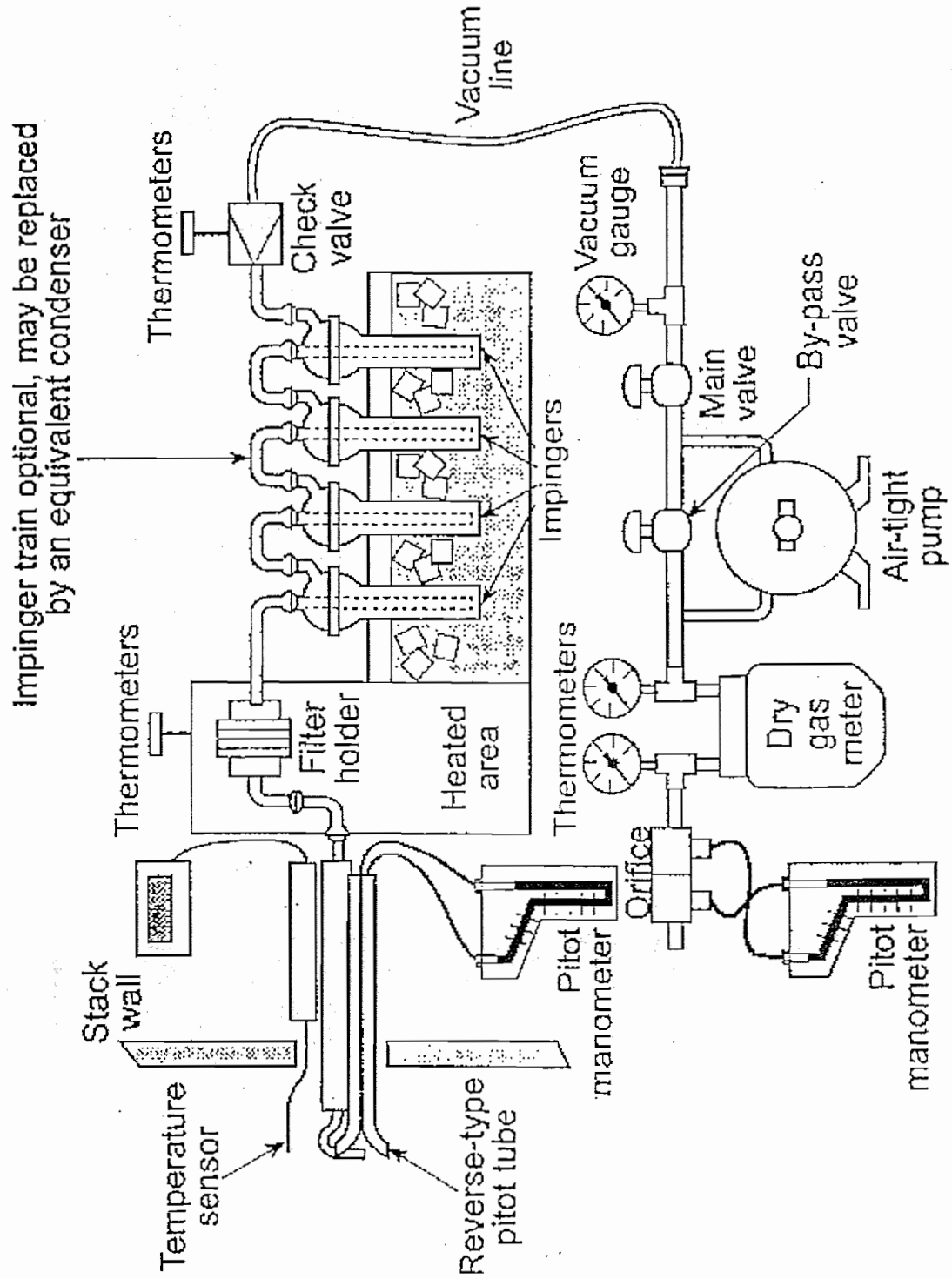
7.2.3.2 Calibrate the metering system according to the procedure outlined in Sections 7.2.2.2.1 to 7.2.2.2.5.

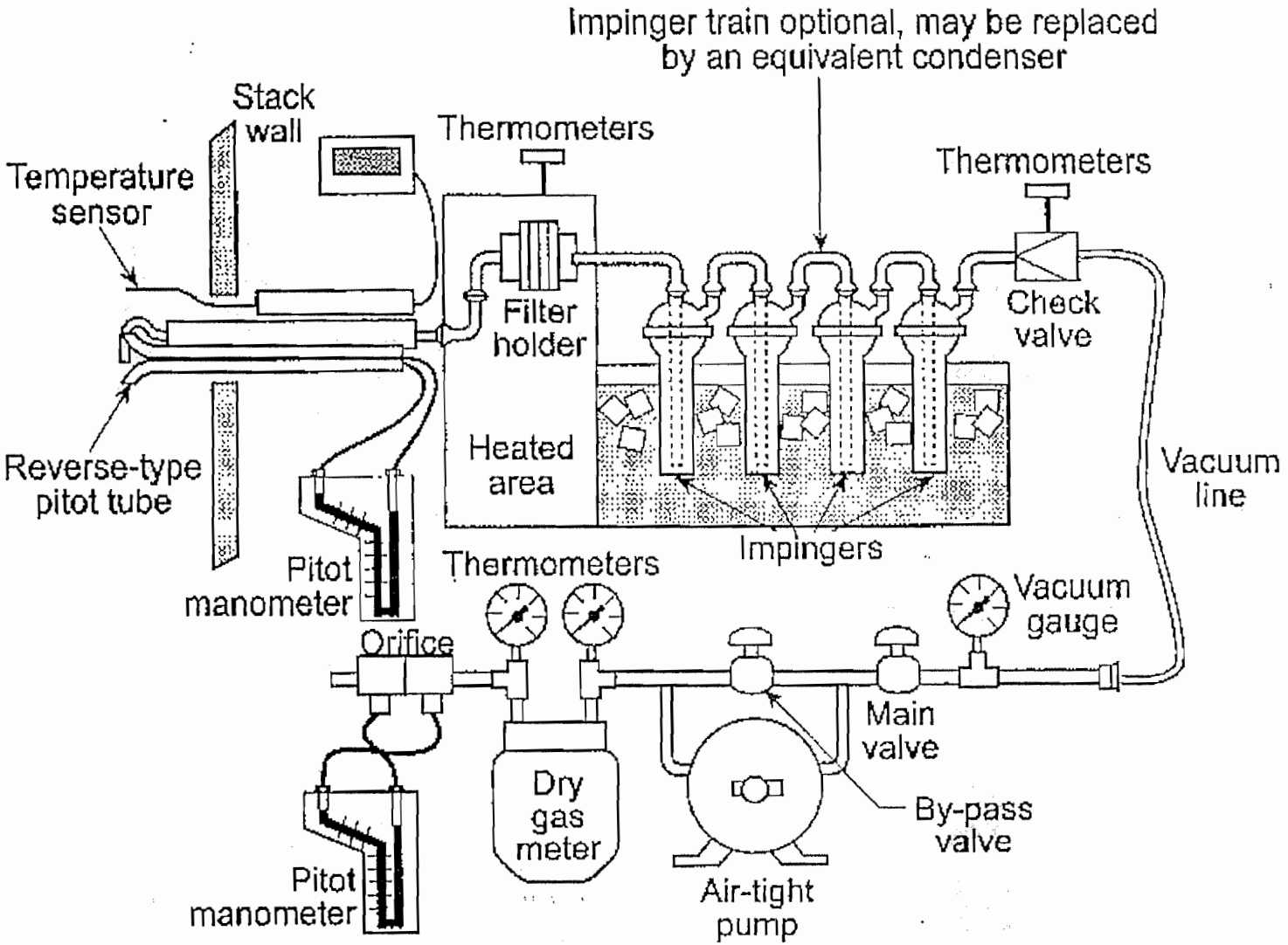
7.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y.

7.2.3.4 Average the DGM calibration values for each of the flow rates.

7.2.3.5 Determine the need for recalibrating the critical orifices.


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
Thermometers
Thermometers
Temperature sensor
Filter holder
Check valve
Heated area
Vacuum line
Reverse-type pitot tube
Impingers
Pitot manometer
Thermometers
Vacuum gauge
Orifice
Main valve
Dry gas meter
By-pass valve
Pitot manometer
Air-tight pump


Impinger train optional, may be replaced by an equivalent condenser
Thermometers
Check valve
Vacuum line
Vacuum gauge
By-pass valve
Main valve
Impingers
Air-tight pump
Thermometers
Filter holder
Heated area
Thermometers
Dry gas meter
Orifice
Stack wall
Pitot manometer
Pitot manometer
Temperature sensor
Reverse-type pitot tube


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
Thermometers
Thermometers
Temperature sensor
Filter holder
Check valve
Heated area
Vacuum line
Reverse-type pitot tube
Impingers
Pitot manometer
Thermometers
Vacuum gauge
Orifice
Main valve
Dry gas meter
By-pass valve
Pitot manometer
Air-tight pump

40 CFR 60 Method 6 (ABRIDGED)

Detection of Sulfur Dioxide Emissions from Stationary Sources

1.0 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, SO_3) and the sulfur dioxide (SO_2) 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 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 mL of 3 percent hydrogen peroxide (H_2O_2), at a rate of 1.0 L/min for 20 minutes. Possible interferants are free ammonia, water-soluble cations, and fluorides. 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 interferants. Free ammonia interferes by reacting with SO_2 to form particulate sulfite and by reacting with the indicator.

2.0 Apparatus

2.1 Sampling

The sampling train is shown in the Figure at the end of this method, 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) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system.

2.1.1 Probe

Borosilicate glass, or stainless steel approximately 6 mm I.D., 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 and three 30 mL midget impingers. The bubbler and midget impingers must be connected in series with leak-free glass connectors.

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°C (2°F).

2.1.6 Drying Tube

Tube packed with 6 to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump.

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.

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 mL/min.

2.1.10 Volume Meter

Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent.

2.1.11 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). The barometric reading may be obtained from a nearby National Weather Service station.

2.1.12 Vacuum Gauge and Rotameter

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

2.2 Sample Recovery

2.2.1 Wash Bottles Polyethylene or glass, 500 mL, two.

2.2.2 Storage Bottles

Polyethylene, 100 mL.

2.3 Analysis

2.3.1 Pipettes

2.3.2 Volumetric Flasks

2.3.3 Burettes

2.3.4 Erlenmeyer Flasks

2.3.5 Dropping Bottle

2.3.6 Graduated Cylinder

2.3.7 Spectrophotometer

3.0 Reagents

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 D1 193-77, Type 3.

3.1.2 Isopropanol, 80 Percent

Mix 80 mL of isopropanol with 20 mL of water. Check each lot of isopropanol for peroxide impurities.

3.1.3 Hydrogen Peroxide, 3 Percent

Dilute 30 percent hydrogen peroxide (H_2O_2) 1:9 (v/v) with water (30 mL is needed per sample).

3.1.4 Potassium Iodide Solution, 10 Percent

Dissolve 10.0 g KI in water and dilute to 100 mL.

3.2 Sample Recovery

3.2.1 Water

Same as in Section 3.1.1.

3.2.2 Isopropanol

80 Percent (mix 80 mL of isopropanol with 20 mL of water).

3.3 Analysis

3.3.1 Water

3.3.2 Isopropanol, 100 Percent

3.3.3 Thorin Indicator

3.3.4 Barium Perchlorate Solution, 0.0100 N

3.3.5 Sulfuric Acid Standard, 0.0100 N

3.3.6 Quality Assurance Audit Samples

3.3.7 Hydrochloric Acid (HCl) Solution, 0.1 N

4.0 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 the Figure at the end of this method. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak Check Procedure

A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory.

Temporarily attach a suitable (e.g., 0-40 mL/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 (110 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump. To leak check the pump, disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

4.1.3 Sample Collection

Record the initial dry gas meter reading and barometric pressure. 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 L/min. 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. 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 water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.2.1 Sample Analysis

4.3 Audit Sample Analysis

5.0 Calibration

5.1 Metering System

5.1.1 Initial Calibration

Before its initial use in the field, first leak check the metering system (drying tubing, needle valve, pump, rotameter, and dry gas meter). The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

Remove the drying tube and calibrate the metering system. Connect an appropriately sized wet test meter 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), and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use.

5.1.2 Post-Test Calibration Check

After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three, or more revolutions of the dry gas meter may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable.

5.2 Thermometers

Calibrate against mercury-in-glass thermometers.

5.3 Rotameter

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

5.4 Barometer

Calibrate against a mercury barometer.

5.5 Barium Perchlorate Solution

Standardize the barium perchlorate solution against 25 mL of standard sulfuric acid to which 100 mL of 100 percent isopropanol has been added.

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

6.0 Calculations

Carry out calculations.

6.1 Nomenclature

6.2 Dry Sample Gas Volume

6.3 Sulfur Dioxide Concentration

6.4 Relative Error (RE) for QA Audit Sample

7.0 Alternative Procedures

7.1 Dry Gas Meter as a Calibration Standard

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

7.2 Critical Orifices for Volume and Rate Measurement

A critical orifice may be used in place of the dry gas meter specified in Section 2.1.10.

7.2.1 Preparation of Collection Train

Prepare the sampling train using the critical orifice. The rotameter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers.

7.2.2 Selection of Critical Orifices

This section describes the use of hypodermic needles and stainless steel needle tubing, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices (i.e., a critical vacuum can be obtained as described in this section. Select a critical orifice that is sized to operate at the desired flow rate). The needle sizes and tubing lengths are discussed in this method.

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

7.2.3 Field Procedure

7.2.3.1 Leak Check Procedure

A leak check before the sampling run is recommended, but is optional. Temporarily attach a suitable (e.g., 0-40 mL/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 254 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable. Carefully release the probe inlet plug before turning off the pump.

7.2.3.2 Moisture Determination

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

7.2.3.3 Critical Orifice Calibration

Prior to testing, at the sampling location, calibrate the entire sampling train using a 500 mL soap bubble meter attached to the inlet of the probe and an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information.

Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate.

7.2.3.4 Sampling

Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously. Conduct a post-test calibration run using the calibration procedure outlined in Section 7.2.3.3. If the Q_{std} obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice and the average of Q_{std} of both runs.

If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more than 3 percent, then the molecular weight of the gas sample must be considered in the calculations.

NOTE: A post-test leak check is not necessary because the post-test calibration run results will indicate whether there is any leakage. Drain the ice bath, and purge the sampling train using the procedure described in Section 4.1.3.

7.3 Elimination of Ammonia Interference

The following alternative procedures shall be used in addition to those specified in the method when sampling at sources having ammonia emissions.

7.3.1 Sampling

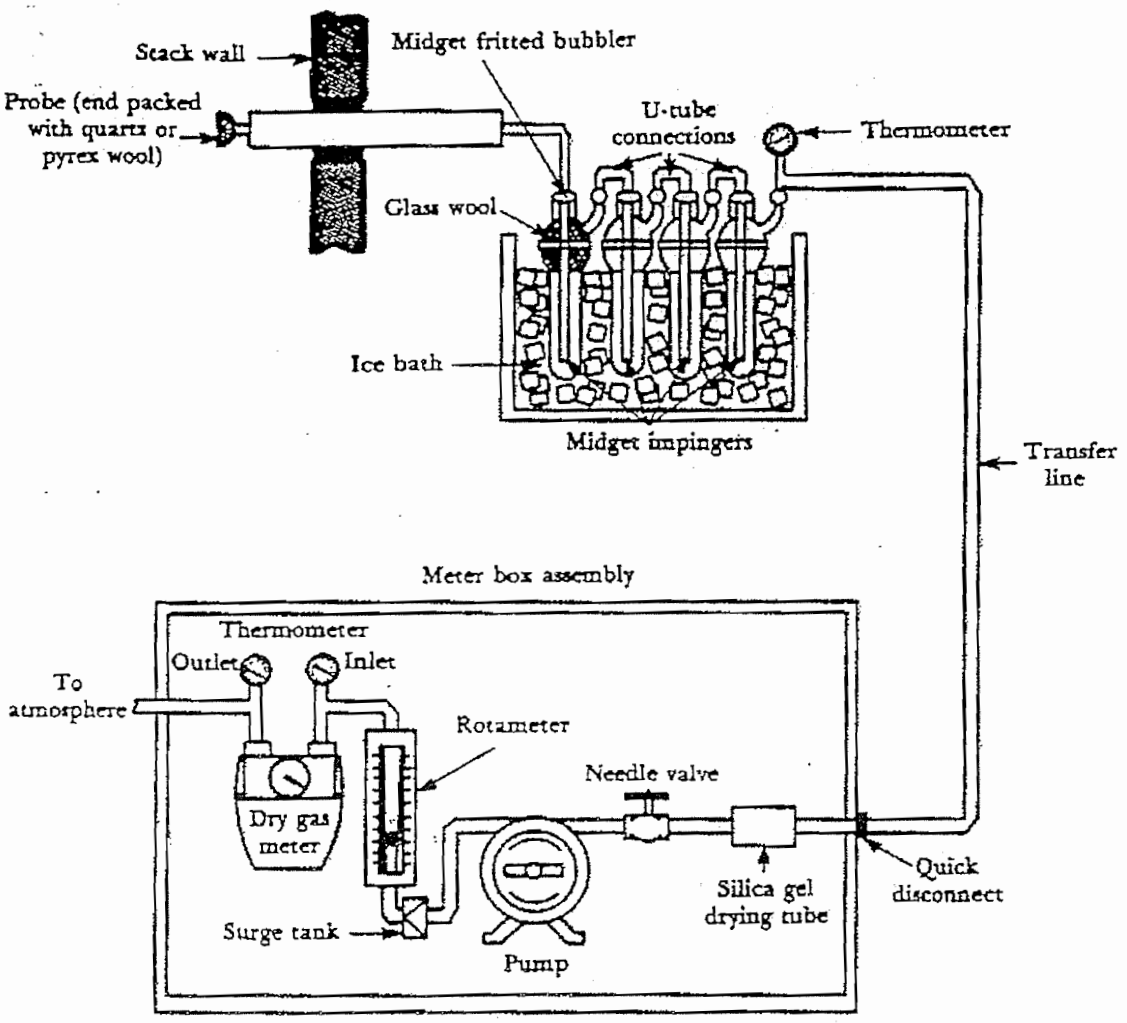
The probe shall be maintained at 275°C and equipped with a high efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO_2. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225°C.

7.3.2 Sample Recovery

Recover the sample according to Section 4.2 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to the polyethylene bottle containing the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

7.3.3 Sample Analysis

8.0 Bibliography


Stack wall
Midget fritted bubbler
Probe (end packed with quartz or pyrex wool)
U-tube connections
Thermometer
Glass wool
Ice bath
Midget impingers
Transfer line
Meter box assembly
Thermometer
Outlet
Inlet
To atmosphere
Rotameter
Needle valve
Dry gas meter
Silica gel drying tube
Quick disconnect
Surge tank
Pump

40 CFR 60, Method 6A (ABRIDGED)

Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide From Fossil Fuel Combustion Sources

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Persons using this method should have a thorough knowledge of the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

1.0 Scope and Application

1.1 Analytes

1.2 Applicability

This method is applicable for the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10^6 Btu) and for the determination of carbon dioxide (CO_2) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Sampling

A gas sample is extracted from a sampling point in the stack. The SO_2 and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions

4.0 Interferences

Same as Method 6, Section 4.0.

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents

Same as Method 6, Section 5.2.

6.0 Equipment and Supplies

6.1 Sample Collection

Same as Method 6, Section 6.1 with some exceptions.

6.1.1 Sampling Train

A schematic of the sampling train used in this method is shown at the end of this method.

6.1.1.1 Impingers and Bubblers

Two 30 mL midget impingers with a 1 mm restricted tip and two 30 mL midget bubblers with unrestricted tips.

6.1.1.2 CO_2 Absorber

A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm, a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20°C (68°F) above the source temperature, but not greater than 120°C (248°F). The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

6.2 Sample Recovery

Same as Method 6, Section 6.2.

6.3 Sample Analysis

Same as Method 6, Section 6.3, with the addition of a balance to measure within 0.05 g.

7.0 Reagents and Standards

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.1 Sample Collection

Same as Method 6, Section 7.1, with some additions.

7.1.1 Drierite

Anhydrous calcium sulfate ($CaSO_4$) desiccant.

Do not use silica gel or similar desiccant in this application.

7.1.2 CO_2 Absorbing Material

Ascarite II. Sodium hydroxide-coated silica, 8 to 20-mesh.

7.2 Sample Recovery and Analysis

Same as Method 6, Sections 7.2 and 7.3, respectively.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train

8.1.1 Sample Train

Measure 15 mL of 80 percent isopropanol into the first midget bubbler and 15 mL of 3 percent hydrogen peroxide into each of the two midget impingers (the second and third vessels in the train) as described in Method 6, Section 8.1. Insert the glass wool into the top of the isopropanol bubbler. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m_{wi}).

8.1.2 CO_2 Adsorber

With one end of the CO_2 absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool.

Assemble the cylinder. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m_{ai}).

8.1.3 Assemble Sampling Train

Assemble the train. Adjust the probe heater to a temperature sufficient to prevent condensation (see NOTE in Section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO_2 absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (e.g., Tygon) may be used to connect the last SO_2 absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed.

8.1.4 Sampling Train Leak Check Procedure and Sample Collection

Same as Method 6, Sections 8.2 and 8.3, respectively.

8.2 Sample Recovery

8.2.1 Moisture Measurement

Disconnect the isopropanol bubbler, the SO_2 impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in Section 8.1. Record this final weight (m_{wf}).

8.2.2 Peroxide Solution

Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.2.3 CO_2 Absorber

Allow the CO_2 absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in Section 8.1. Record this final weight (m_{af}). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, Section 9.0.

10.0 Calibration and Standardization

Same as Method 6, Section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis

The sample analysis procedure for SO_2 is the same as that specified in Method 6, Section 11.0.

11.2 Quality Assurance (QA)

Audit Samples. Analysis of QA audit samples is required only when this method is used for compliance determinations.

12.0 Data Analysis and Calculations

Same as Method 6, Section 12.0.

13.0 Method Performance

14.0 Range and Precision

The minimum detectable limit and the upper limit for the measurement of SO_2 are the same as for Method 6.

15.0 Pollution Prevention

16.0 Waste Management

17.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J or $lb/10^6$ Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

17.1 Sampling Train

The sampling train is the same as that described in Section 6.1, except that the dry gas meter is not needed.

17.2 Preparation of the Sampling Train

Follow the same procedure as in Section 8.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

17.3 Sampling Train Leak Check Procedure and Sample Collection

Leak check and operate the sampling train as described in Section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

17.4 Sample Recovery

Follow the procedure in Section 8.3, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

17.5 Sample Analysis

Analysis of the peroxide solution and QA audit samples is the same as that described in Sections 11.1 and 11.2, respectively.

17.6 Calculations

18.0 References

19.0 Tables, Diagrams, Flowcharts, and Validation Data.

40 CFR 60, Method 6B (ABRIDGED)

Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emissions from Fossil Fuel Combustion Sources

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Persons using this method should have a thorough knowledge of the following test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes

1.2 Applicability

This method is applicable for the determination of SO_2 emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10^6 Btu), and for the determination of CO_2 concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Sampling

A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO_2 fraction is measured by the barium-thorin titration method. Moisture and CO_2 fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions

4.0 Interferences

Same as Method 6, Section 4.0.

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents

Same as Method 6, Section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, Section 6.0, with some exceptions.

6.1 Isopropanol Bubbler

The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets , that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 Industrial Timer-switch

For intermittent operation, include an industrial timer-switch designed to operate in the "on" position at least 2 minutes continuously and "off" the remaining period over a repeating cycle. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Sampling Probes

Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, e.g., Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

7.0 Reagents and Standards

Same as Method 6A, Section 7.0, with some exceptions.

7.1 Isopropanol

Isopropanol is not used for sampling.

7.2 Hydrogen Peroxide

The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 Sampling Rate

If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 mL/min or 0.21 ft^3/hr), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train

Same as Method 6A, Section 8.1, with some addition.

8.1.1 Isopropanol Bubbler

The sampling train is assembled as shown in Figure 6A-1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Sampling Time

Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation.

8.1.3 Cold Water Addition

Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

8.2 Sampling Train Leak Check Procedure

Same as Method 6, Section 8.2.

8.3 Sample Collection

8.3.1 Operating Temperature of Probe and Filter

The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Sampling

Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 L/min (0.035 cfm) as indicated by the rotameter.

8.3.3 Field Data Recording

One time between 9:00 a.m. and 11:00 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure ($P_{(bar)}$).

8.3.4 Recovery/Leak check

At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak check.

8.4 Sample Recovery

The procedures for sample recovery (moisture measurement, peroxide solution, and CO_2 absorber) are the same as those in Method 6A, Section 8.3.

9.0 Quality Control

Same as Method 6, Section 9.0, with the exception of the isopropanol check.

10.0 Calibration and Standardization

Same as Method 6, Section 10.0, with the addition of the following.

10.1 Periodic Calibration Check

After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, Section 10.1.2).

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis

Same as Method 6, Sections 11.1 and 11.2, respectively.

11.2 Quality Assurance (QA) Audit Samples

Analysis of QA audit samples is required only when this method is used for compliance determinations.

12.0 Data Analysis and Calculations.

Same as Method 6A, Section 12.0, except that P_{bar} and T_m correspond to the values recorded in Section 8.3.3 of this method.

13.0 Method Performance.

13.1 Range.

13.1.1 Sulfur Dioxide.

Same as Method 6.

13.1.2 Carbon Dioxide

Not determined.

13.2 Repeatability and Reproducibility

EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention

15.0 Waste Management

16.0 Alternative Methods

Same as Method 6A, Section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

18.0 Tables, Diagrams, Flowcharts, and Validation Data

40 CFR 60, Method 6C (ABRIDGED)

Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure)

1.0 Principle and Applicability

1.1 Principle

1.2 A gas sample is continuously extracted from the stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO_2 gas concentration using an ultraviolet (UV), non-dispersive infrared (NDIR), or fluorescence analyzer.

1.3 Applicability

This method is applicable to the determination of sulfur dioxide (SO_2) concentrations in controlled and uncontrolled emissions from stationary sources.

2.0 Range and Sensitivity

2.1 Analytical Range

The analytical range is determined by the instrument design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system.

2.2 Sensitivity

The minimum detectable limit should be less than 2 percent of the span.

3.0 Measurement System Performance Specifications

3.1 Analyzer Calibration Error

Less than ± 2 percent of the span for the zero, mid-range, and high-range calibration gases.

3.2 Sampling System Bias

Less than ± 5 percent of the span for the zero, and mid- or high-range calibration gases.

3.3 Zero Drift

Less than ±3 percent of the span over the period of each run.

3.4 Calibration Drift

Less than ± 3 percent of the span over the period of each run.

3.5 Interference Check

Less than ±7 percent of the modified Method 6 result for each run.

4.0 Apparatus and Reagents

4.1 Measurement System

Any measurement system for SO_2 that meets the specifications of this method. The essential components of the measurement system are provided below.

4.1.1 Sample Probe

Glass, stainless steel, or equivalent, of sufficient length to traverse the sample points.

4.1.2 Sample Line

Heated (sufficient to prevent condensation) stainless steel or Teflon tubing.

4.1.3 Sample Transport Lines

Stainless steel or Teflon tubing.

4.1.4 Calibration Valve Assembly

A three-way valve assembly for blocking the sample gas flow and introducing calibration gases to the measurement system.

4.1.5 Moisture Removal System

A refrigerator-type condenser to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas.

4.1.6 Particulate Filter

An in-stack or heated out-of-stack filter. The filter shall be borosilicate or quartz glass wool, or glass fiber mat.

4.1.7 Sample Pump

A leak-free pump. The pump may be constructed of any material that is non-reactive to the gas being sampled.

4.1.8 Sample Flow Rate Control

A sample flow rate control valve and rotameter.

4.1.9 Sample Gas Manifold

A sample gas manifold, to divert a portion of the sample gas stream to the analyzer, and the remainder to the by-pass discharge vent.

4.1.10 Gas Analyzer

A UV-NDIR absorption analyzer, to determine the SO_2 concentration in the sample gas stream continuously.

4.1.11 Data Recorder

A strip chart recorder, analog computer, or digital recorder, for recording measurement data.

4.2 Method 6C Apparatus and Reagents

The apparatus and reagents described in Method 6, and shown by the schematic of the sampling train.

4.3 SO_2 Calibration Gases

The calibration gases for the gas analyzer shall be SO_2 in N_2 or SO_2 in air. Alternatively, gas mixtures in N_2 may be used.

4.3.1 High-Range Gas

Concentration equivalent to 80 to 100 percent of the span.

4.3.2 Mid-Range Gas

Concentration equivalent to 40 to 60 percent of the span.

4.3.3 Zero Gas

Concentration of less than 0.25 percent of the span.

5.0 Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions.

5.1 Calibration Gas Concentration Verification

There are two alternatives for establishing the concentrations of calibration gases. Alternative Number 1 is preferred.

5.1.1 Alternative Number 1

Use of calibration gases that are analyzed following the EPA Traceability Protocol Number 1.

5.1.2 Alternative Number 2

Use of calibration gases not prepared according to Protocol Number 1. If this alternative is chosen, obtain gas mixtures with a manufacturer's tolerance not to exceed 2 percent of the tag value.

5.2 Measurement System Preparation

Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer.

5.3 Analyzer Calibration Error

Conduct the analyzer calibration error check by introducing calibration gases to the measurement system.

5.3.1 Introduction of Gases

After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer.

5.3.2 Invalid Calibration Error Check

The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds ± 2 percent of the span for any of the calibration gases.

5.4 Sampling System Bias Check

Perform the sampling system bias check.

5.4.1 Introduction of Gas

Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer. Then introduce zero gas, and record the gas concentration displayed by the analyzer.

5.4.2 Invalid System Bias Check

The sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the analyzer calibration error check and for the sampling system bias check exceeds 5 percent of the span for either the zero or upscale calibration gas.

6.0 Emission Test Procedure

6.1 Selection of Sampling Site and Sampling Points

Select a measurement site and sampling points using the same criteria that are applicable to Method 6.

6.2 Interference Check Preparation

For each individual analyzer, conduct an interference check for at least three runs.

6.3 Sample Collection

Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check.

6.4 Zero and Calibration Drift Tests

Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in Section 6.4.

6.4.1 Invalid Run

If either the zero or the calibration value

exceeds the sampling system bias specification, then the run is considered invalid.

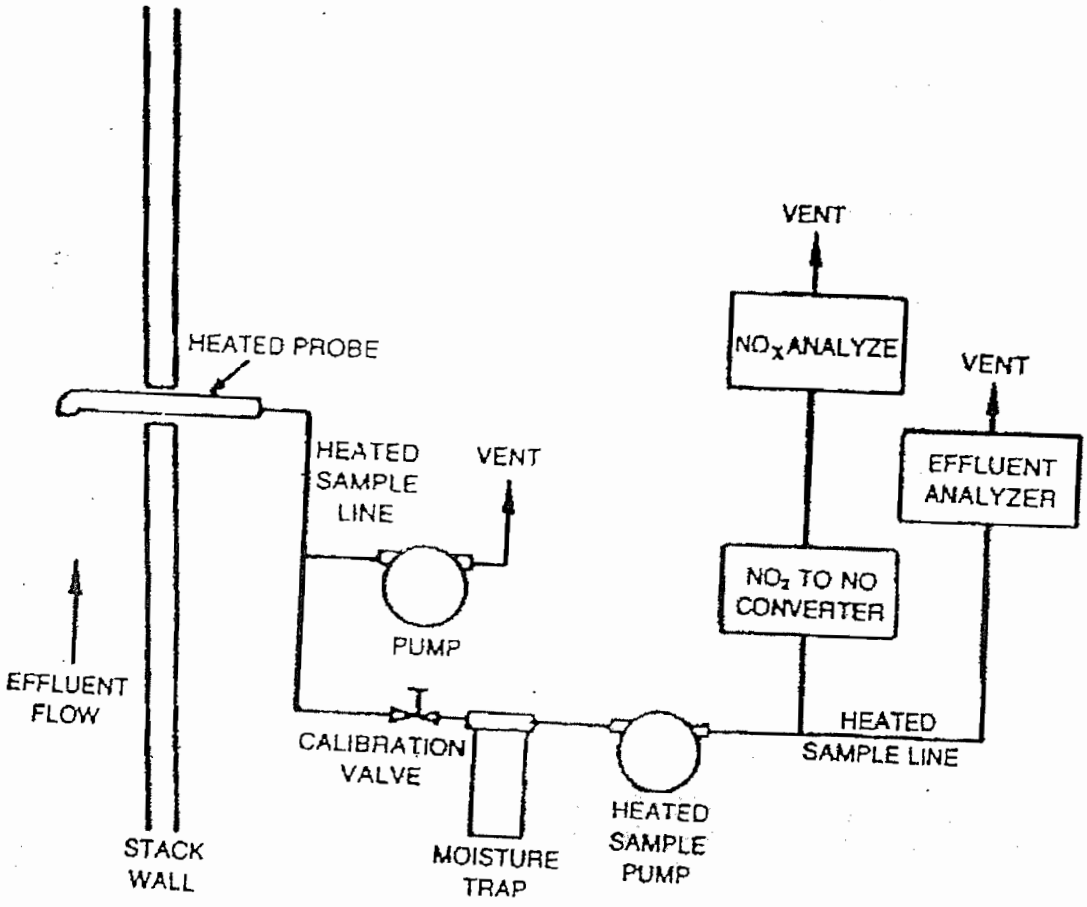
6.4.2 Average Bias Check Calculation

If both the zero and upscale calibration values are within the sampling system bias specification, use the average of the initial and final bias check values to calculate the gas concentration for the run.

6.5 Interference Check (if Performed)

After completing the run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers, and determine the SO_2 gas concentration using the procedures of Method 6. Emission Calculation

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer, and is adjusted for the zero and upscale sampling system bias checks.


VENT
HEATED PROBE
NO_X ANALYZE
VENT
HEATED SAMPLE LINE
VENT
EFFLUENT ANALYZER
NO_2 TO NO CONVERTER
PUMP
EFFLUENT FLOW
CALIBRATION VALVE
HEATED SAMPLE LINE
HEATED SAMPLE PUMP
STACK WALL
MOISTURE TRAP

40 CFR 60, Method 7 (ABRIDGED)

Determination of Nitrogen Oxide Emissions From Stationary Sources

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Persons using this method should have a thorough knowledge of the following test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Principle

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

1.2 Applicability.

This method is applicable for the measurement of nitrogen oxides (NO_x) emitted from stationary sources.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Apparatus

2.1 Sample Collection.

The following items are required for sample collection:

2.1.1 Probe

Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose).

2.1.2 Collection Flask

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

2.1.3 Flask Valve.

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

2.1.4 Temperature Gauge

Dial-type thermometer, or other temperature gauge, capable of measuring 1°C (2°F) intervals from -5 to 50°C (23 to 122°F).

2.1.5 Vacuum Line.

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

2.1.6 Vacuum Gauge.

U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

2.1.7 Pump

Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (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.

2.1.11 Barometer.

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See NOTE in Method 5.

2.2 Sample Recovery. The following items are 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

2.3.1 Volumetric Pipettes

Two 1 mL, two 2 mL, one 3 mL, one 4 mL, two 10 mL, and one 25 mL for each sample and standard.

2.3.2 Porcelain Evaporating Dishes.

175 to 250 mL capacity with lip for pouring, one for each sample and each standard.

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 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.

3.0 Reagents

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

3.1 Sampling

Prepare the absorbing solution.

3.2 Sample Recovery

The following reagents are required for sample recovery:

3.2.1 Sodium Hydroxide, 1 N

Dissolve 40 g NaOH in water, and dilute to 1 liter.

3.2.2 Water

ASTM Specification D1193-77, Type 3

3.3 Analysis

The following reagents and standards are required for analysis:

3.3.1 Fuming Sulfuric Acid

15 to 18 percent by weight free sulfur trioxide..

3.3.2 Phenol

White solid.

3.3.3 Sulfuric Acid

Concentrated, 95 percent minimum assay.

3.3.4 Potassium Nitrate (KNO_3)

Dried at 105 to 110°C (221 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 KNO_3 in water, and dilute to 1 liter with water in a 1000-mL volumetric flask.

3.3.6 Working Standard KNO_3 Solution

Dilute 10 mL of the standard solution to 100 mL with water.

3.3.7 Phenoldisulfonic Acid Solution.

Dissolve 25 g of pure white phenol solid in 150 mL concentrated sulfuric acid on a steam bath. Cool, add 75 mL fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide - HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

3.3.8 Concentrated Ammonium Hydroxide.

3.3.9 Quality Assurance Audit Samples

When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA Regional Office.

4.0 Procedures

4.1 Sampling

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 and place the probe at the sampling point..

4.1.1 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 , then introduce oxygen into the flask to permit this conversion.

4.2 Sample Recovery

Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer.

4.3 Analysis.

4.4 Audit Sample Analysis.

Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

5.0 Calibration

5.1 Flask Volume

5.2 Spectrophotometer.

5.2.1 Optimum Wavelength Determination.

Calibrate the wavelength scale of the spectrophotometer every 6 months.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c

5.2.3 Spectrophotometer Calibration Quality Control.

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.

5.6 Analytical Balance

Calibrate against standard weights.

6.0 Calculations.

Carry out the calculations.

6.1 Nomenclature

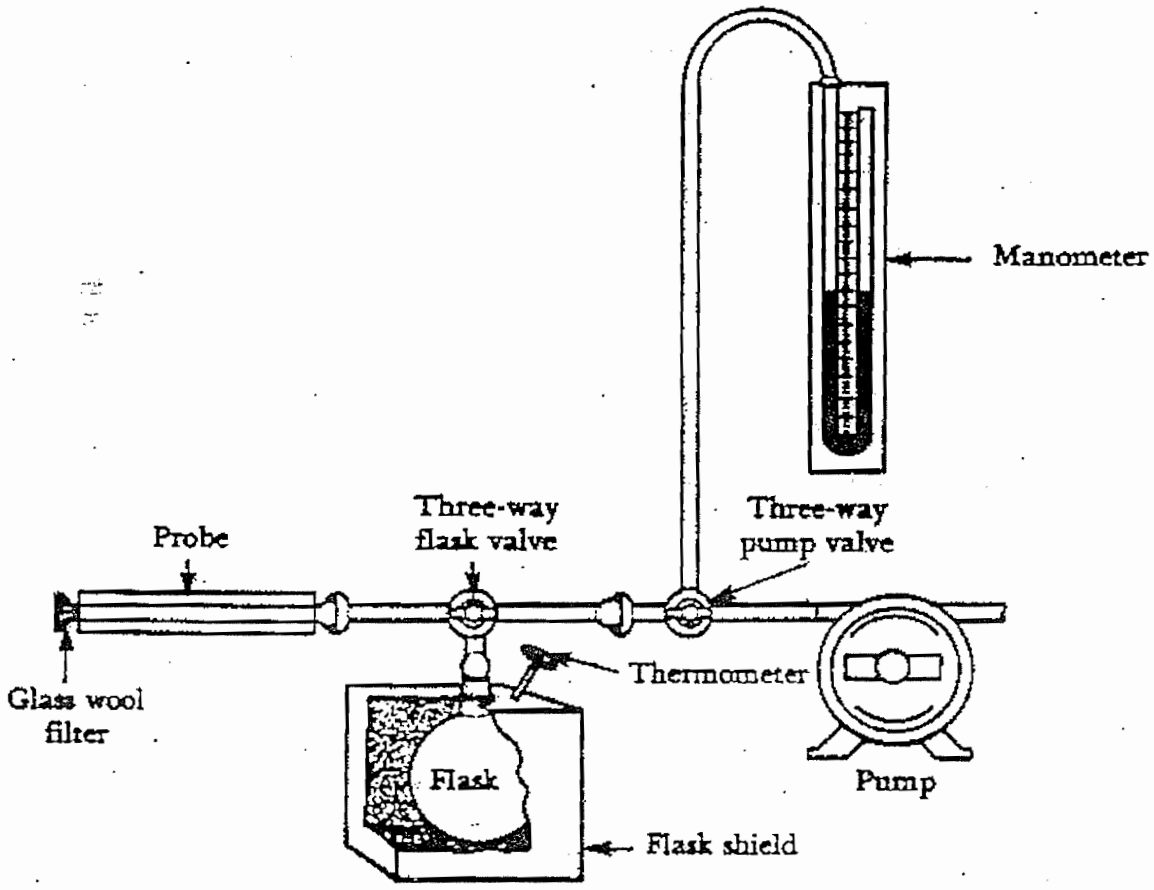
6.2 Sample Volume, Dry Basis, Corrected to Standard Conditions.

6.3 Total μg NO_2 per sample.

6.4 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

6.5 Relative Error for QA Audit Samples.

7.0 Bibliography


Manometer
Three-way
flask valve
Three-way
pump valve
Probe
Thermometer
Glass wool
filter
Flask
Pump
Flask shield

40 CFR 60, Method 7E (ABRIDGED)

Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrument Analyzer Procedure)

1.0 Principle and Applicability

1.1 Principle

A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental chemiluminescent analyzer for determination of NO_x concentration.

1.2 Applicability

This method is applicable to the determination of nitrogen oxide (NO) concentrations in emissions from stationary sources.

2.0 Range and Sensitivity

Same as Method 6C.

3.0 Definitions

3.1 Measurement System

The total equipment required for the determination of NO_x concentration consists of the following major subsystems.

3.1.1 Sample Interface, Gas Analyzer, and Data Recorder

Same as Method 6C.

3.1.2 NO_2 to NO Converter

A device that converts the nitrogen dioxide (NO_2) in the sample gas to nitrogen oxide (NO).

3.2 Span, Calibration Gas, Analyzer Calibration Error, Sampling System Bias, Zero Drift, Calibration Drift, and Response Time

Same as Method 6C, Sections 3.2 through 3.8.

3.3 Interference Response

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

4.0 Measurement System Performance Specifications

Same as Method 6C.

5.0 Apparatus and Reagents

5.1 Measurement System

Any measurement system for NO, that meets the specifications of this method. Essential components of the measurement system are described below.

5.1.1 Sample Probe, Sample line, Calibration Valve Assembly, Moisture Removal System, Particulate Filter, Sample Pump, Sample Flow Rate Control, Sample Gas Manifold, and Data Recorder

Same as Method 6C.

5.1.2 NO_2 to NO Converter

That portion of the system that converts the nitrogen dioxide (NO_2) in the sample gas to nitrogen oxide (NO).

5.1.3 NO_x Analyzer

An analyzer based on the principles of chemiluminescence, to determine the NO_X concentration in the sample gas stream continuously.

5.2 NO_X Calibration Gases

The calibration gases for the NO_X analyzer shall be NO in N_2. Three calibration gases, as specified in Method 6C, shall be used. Ambient air may be used for the zero gas.

6.0 Measurement System Performance Test Procedures

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

6.1 Calibration Gas Concentration Verification

Follow Section 6.1 of Method 6C, except, if calibration gas analysis is required, use Method 7, and change all 5 percent performance values to 10 percent (or 10 ppm, whichever is greater).

6.2 Interference Response

Conduct an interference response test of the analyzer prior to its initial use in the field.

6.3 Measurement System Preparation, Analyzer Calibration Error, and Sample System Bias Check

Follow Sections 6.2 through 6.4 of Method 6C.

6.4 NO_2 to NO Conversion Efficiency

Unless data are presented to demonstrate that the NO_2 concentration within the sample stream is not greater than 5 percent of the NO_X concentration, conduct an NO_2 to NO conversion efficiency test in accordance with Section 5.6 of Method 20.

7.0 Emission Test Procedure

7.1 Selection of Sampling Site and Sampling Points

Select a measurement site and sampling points using the same criteria that are applicable to tests performed using Method 7.

7.2 Sample Collection

Position the sampling probe at the first measurement point, and begin sampling.

7.3 Zero and Calibration Drift Test

Follow Method 6C.

8.0 Emission Calculation

Follow Method 6C.

40 CFR 60, Method 8 (ABRIDGED)

Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions From Stationary Sources

1.0 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 and sulfur dioxide emissions from stationary sources.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline.

Filterable particulate matter may be determined along with SO_3 and SO_2, (subject to the approval of the Administrator).

2.0 Apparatus

2.1 Sampling

A schematic of the sampling train used in this method is is similar to the Method 5 train except that the filter position is different and the filter holder does not have to be heated.

2.1.1 Probe Nozzle

Same as Method 5.

2.1.2 Probe Liner

Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling.

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.

2.1.6 Impingers

Four, the first and third shall be of the Greenburg-Smith design with standard tips. The second and fourth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 mm (0.5 in.) I.D. glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask.

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, to measure the temperature of the gas leaving the impinger train.

2.2 Sample Recovery

2.2.1 Wash Bottles

Polyethylene or glass, 500 mL (two).

2.2.2 Graduated Cylinders

250 mL, 1 L.

2.2.3 Storage Bottles

Leak-free polyethylene bottles, 1000 mL size (two for each sampling run).

2.2.4 Trip Balance

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

2.3 Analysis

2.3.1 Pipettes

2.3.2 Burette

2.3.3 Erlenmeyer Flask

2.3.4 Graduated Cylinder

2.3.5 Trip Balance

2.3.6 Dropping Bottle

3.0 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 Silca Gel

Same as Method 5, Section 3.1.2.

3.1.3 Water

Deionized, distilled to conform to ASTM Specification D1 193-77, Type 3.

3.1.4 Isopropanol, 80 Percent

Mix 800 mL of isopropanol with 200 mL of deionized, distilled water.

3.1.5 Hydrogen Peroxide

3 Percent Dilute 100 mL of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water.

3.1.6 Crushed Ice

3.2 Sample Recovery

3.2.1 Water

Same as Section 3.1.3.

3.2.2 Isopropanol, 80 Percent

Same as 3.1.4.

3.3 Analysis

3.3.1 Water

3.3.2 Isopropanol

3.3.3 Thorin Indicator

3.3.4 Barium Perchlorate (0.0100 N)

3.3.5 Sulfuric Acid Standard (0.0100 N)

3.3.6 Quality Assurance Audit Samples

4.0 Procedure

4.1 Sampling

4.1.1 Pretest Preparation

Follow the procedure outlined in Method 5, Section 4.1.1.

4.1.2 Preliminary Determinations

Follow the procedure outlined in Method 5.

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). 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.

4.1.4 Pretest Leak Check Procedure

Follow the basic procedure outlined in Method 5.

4.1.5 Train Operation

Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with special instructions.

4.1.6 Calculation of Percent Isokinetic

Follow the procedure outlined in Method 5.

4.2 Sample Recovery

4.2.1 Container No. 1

If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g and record this weight.

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

Mark the level of liquid on the container and identify the sample container.

4.2.2 Container No. 2

If a moisture content analysis is to be done, weigh the second and third impingers (plus contents) to the nearest 0.5 g and record these weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g. Transfer the solutions from the second

and third impingers to a 1000 mL graduated cylinder.

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

4.3 Analysis

4.3.1 Container No. 1

4.3.2 Container No. 2

4.3.3 Blanks

4.4 Quality Control Procedures

Same as in Method 5, Section 4.4.

4.5 Audit Sample Analysis

Same as in Method 6, Section 4.4.

5.0 Calibration

5.1 Calibrate Equipment

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). The recommended leak check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2 Standardization

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

6.0 Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data.

Round off figures afterfinal calculation.

6.1 Nomenclature

6.2 Average Dry Gas Meter Temperature and

6.2.1 Average Orifice Pressure Drop

6.3 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in. Hg).

6.4 Volume of Water Vapor and Moisture Content

Calculate the volume of water vapor using equation from 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 1.0g/mL).

Calculate the moisture content of the stack gas, using equation from Method 5. The "Note" in Section 6.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric Acid Mist (including SO_3) Concentration

6.6 Sulfur Dioxide Concentration

6.7 Isokinetic Variation

6.7.1 Calculation from Raw Data

6.7.2 Calculation from Intermediate Values

6.8 Acceptable Results

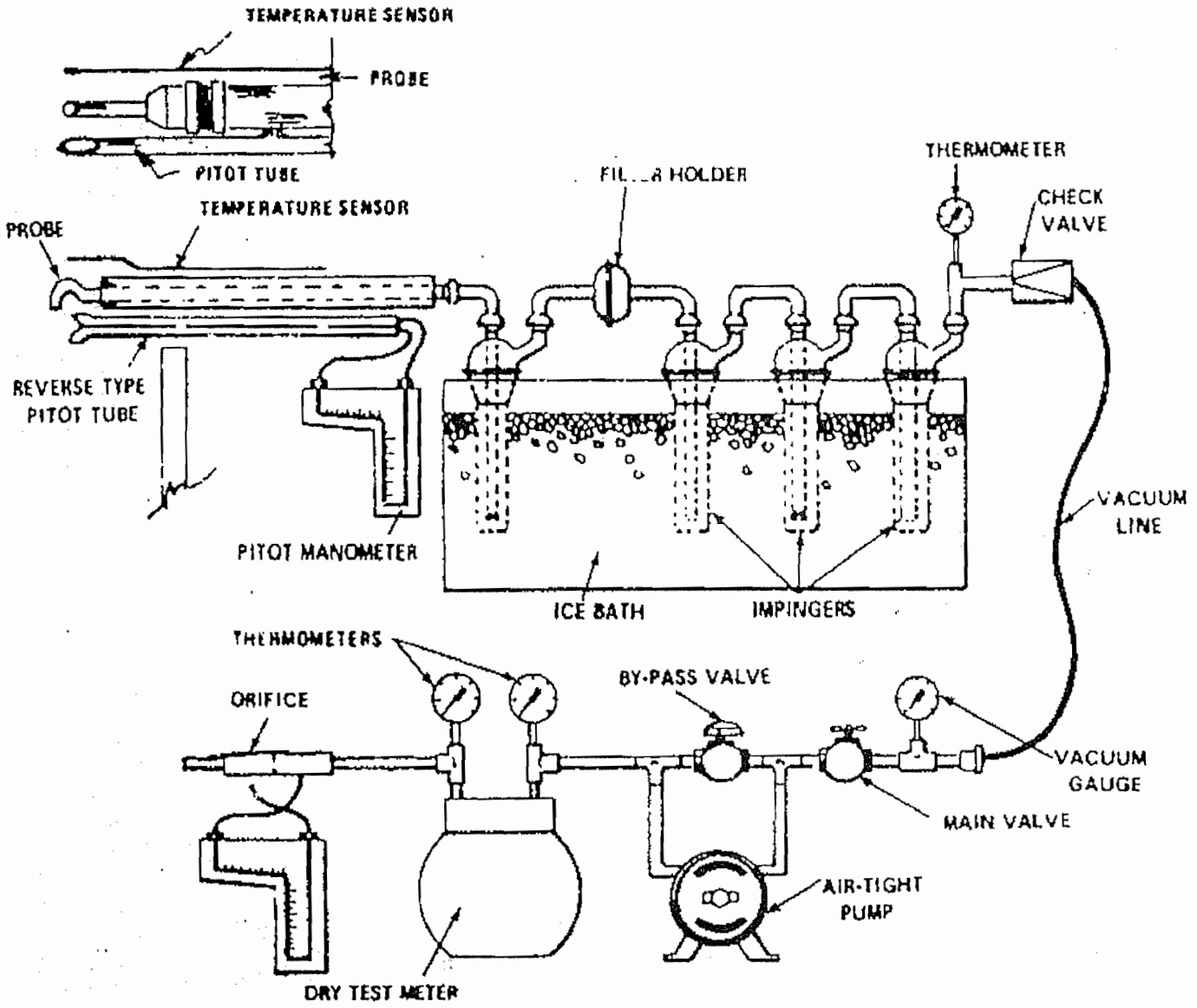
If 90 percent < I <110 percent, the results are acceptable.

6.9 Stack Gas Velocity and Volumetric Flow Rate

Calculate the average stack gas velocity and volumetric flow rate.

6.10 Relative Error (RE) for QA Audit Samples

Same as in Method 6.


TEMPERATURE SENSOR
PROBE
PITOT TUBE
PROBE
TEMPERATURE SENSOR
REVERSE TYPE
PITOT TUBE
PITOT MANOMETER
FILTER HOLDER
THERMOMETER
CHECK
VALVE
VACUUM
LINE
ICE BATH
IMPINGERS
THERMOMETERS
ORIFICE
BY-PASS VALVE
VACUUM
GAUGE
MAIN VALVE
AIR-TIGHT
PUMP
DRY TEST METER

40 CFR 60, Method 11 (ABRIDGED)

Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries

1.0 Scope and Application.

1.1 Principle

A sample is extracted from a source and passed through a series of midget impingers containing a cadmium sulfate ($CdSO_4$) solution; H_2S is absorbed, forming cadmium sulfide (CdS). The latter compound is then measured iodometrically.

1.2 Applicability

This method is applicable for the determination of the H_2S content of fuel gas streams at petroleum refineries.

2.0 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).

3.0 Interferences.

Any compound that reduces iodine (I_2) or oxidizes the iodide ion will interfere in this procedure, provided it is collected in the $CdSO_4$ impingers.

4.0 Precision and Accuracy

Collaborative testing has shown the intra-laboratory precision to be 2.2 percent and the inter-laboratory precision to be 5 percent.

5.0 Apparatus

5.1 Sampling Line

Teflon tubing, 6 to 7 mm (1/4 in.) I.D., to connect the sampling train to the sampling valve.

5.1.1 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.

5.1.2 Tubing

Glass or Teflon connecting tubing for the impingers.

5.1.3 Ice Water Bath

To maintain absorbing solution at a low temperature.

5.1.4 Drying Tube

Tube packed with 6 to 16-mesh indicating-type silica gel.

5.1.5 Sampling Valve

Needle valve, or equivalent, to adjust gas flow rate.

5.1.6 Volume Meter

Dry gas meter (DGM), sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate

5.1.7 Rate Meter

Rotameter, or equivalent, to measure flow rates in the range from 0.5 to 2 liters/min (1 to 4 ft^3/hr).

5.1.8 Graduated Cylinder

25 mL size.

5.1.9 Barometer

5.1.10 U-tube Manometer

5.1.11 Rubber Squeeze Bulb

5.1.12 Tee, Pinch Clamp, and Connecting Tubing.

5.1.13 Pump

Diaphragm pump, or equivalent

5.1.14 Needle Valve or Critical Orifice.

5.1.15 Tube Packed with Active Carbon.

5.1.16 Volumetric Flask

One 1000-mL.

5.1.17 Volumetric Pipette

5.1.18 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.

5.1.19 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.

5.2 5.2 Sample Recovery

5.2.1 Sample Container

Iodine flask, glass-stoppered, 500 mL size.

5.2.2 Volumetric Pipette

5.2.3 Graduated Cylinders

5.2.4 Erlenmeyer Flasks

5.2.5 Wash Bottle.

5.2.6 Volumetric Flasks

5.3 Sample Analysis

5.3.1 Flask

Glass-stoppered iodine flask, 500 mL.

5.3.2 Burette

50 mL.

5.3.3 Erlenmeyer Flask

5.3.4 Volumetric Pipettes

5.3.5 Volumetric Flasks

5.3.6 Graduated Cylinders

6.0 Reagents and Standards.

NOTE: 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.

6.1 Sample

6.1.1 $CdSO_4$ Absorbing Solution

6.1.2 Hydrogen Peroxide, 3 Percent.

6.1.3 Water

Deionized distilled to conform to ASTM D 1193-77.

6.2 Sample Recovery

6.2.1 Water

6.2.2 Hydrochloric Acid (HCl) Solution, 3 M.

6.2.3 Iodine (I_2) Solution, 0.1 N.

6.2.4 Standard I_2 Solution, 0.01 N.

6.3 Sample Analysis

6.3.1 Water

6.3.2 Standard Sodium Thiosulfate Solution, 0.1 N

6.3.3 Standard Sodium Thiosulfate Solution, 0.01 N

6.3.4 Standard Phenylarsine Oxide Solution, 0.01 N

6.3.5 Starch Indicator Solution.

7.0 Procedure

7.1 Sampling

7.1.1 Sampling Train

7.1.2 Leak Check Procedure.

7.1.3 Purging Sampling Train

7.1.4 Sample Rate

7.1.5 Sampling

Sample for at least 10 minutes.

7.1.6 Disconnect

7.2 Sample Recovery.

7.2.1 Discard

Discard the contents of the H_2O_2 impinger.

7.2.2 Pipette

7.2.3 Flask Standing

7.2.4 Blank Analysis

7.3 Analysis

7.3.1 Titration

7.3.2 Blank Titration

8.0 Calibration and Standardization.

8.1 Standardization

8.1.1 Iodine Solution Standardization.

8.1.2 Sodium Thiosulfate Solution Standardization

8.1.3 Phenylarsine Oxide Solution Standardization

8.2 Sampling Train Calibration

8.2.1 Dry Gas Meter.

8.2.1.1 Initial Calibration

The DGM shall be calibrated before its initial use in the field.

8.2.1.2 Post-Test Calibration Check.

After each field test series, conduct a calibration check.

8.2.2 Temperature Sensors

Calibrate against mercury-in-glass thermometers.

8.2.3 Rate Meter

The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

8.2.4 Barometer

Calibrate against a mercury barometer.

9.0 Calculations

Carry out calculations.

9.1 Normality of the Standard (~0.1 N) Sodium Thiosulfate Solution

9.2 Normality of Standard Phenylarsine Oxide Solution

9.3 Normality of Standard Iodine Solution.

9.4 Dry Gas Volume.

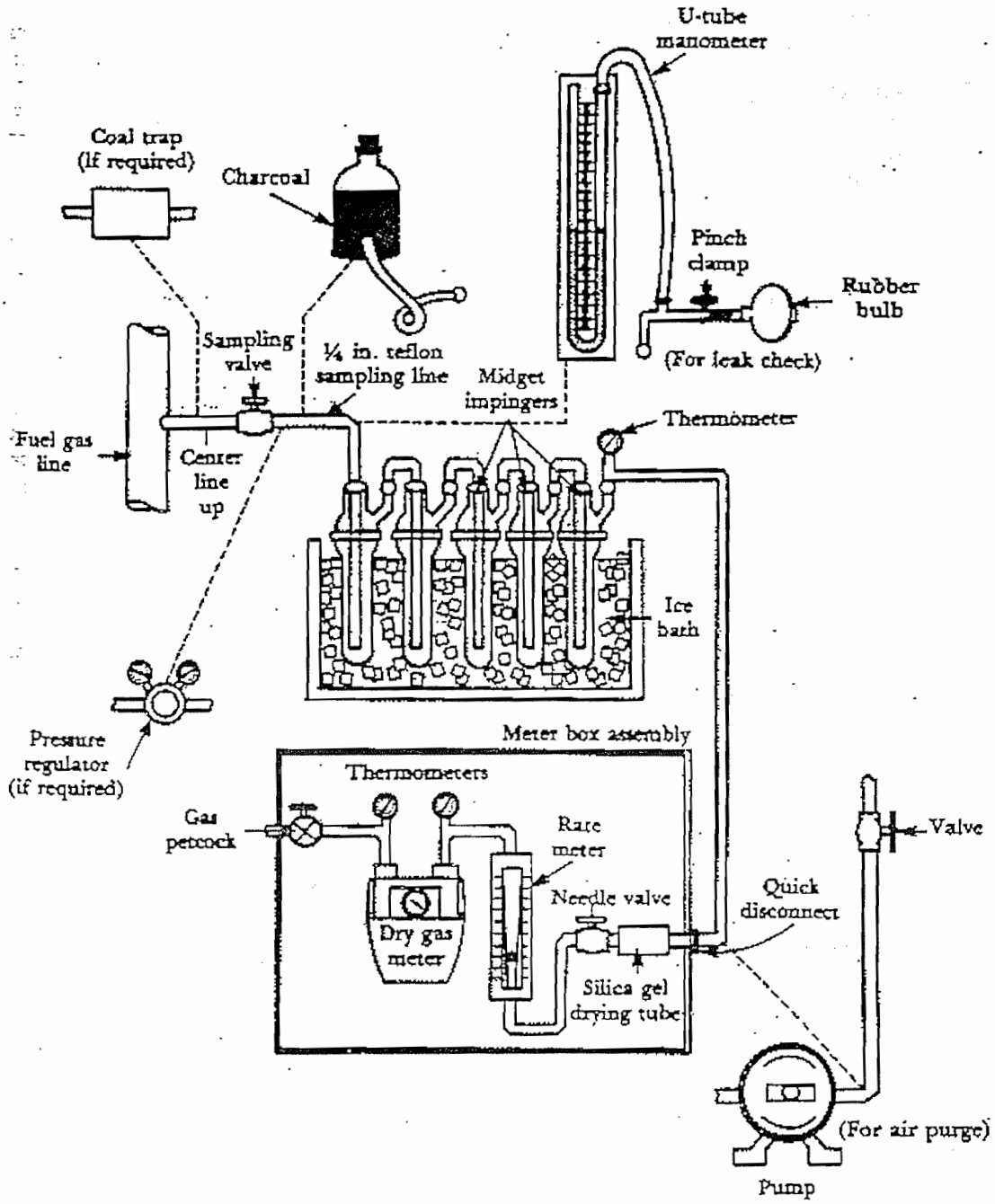
Correct the sample volume measured by the DGM to standard conditions (20°C and 760 mm Hg).

9.5 Concentration of H_2S

Calculate the concentration of H_2S in the gas stream at standard conditions.

10.0 Stability

11.0 References.


U-tube manometer
Coal trap (If required)
Charcoal
Pinch clamp
Rubber bulb
(For leak check)
Sampling valve
¼ in. teflon sampling line
Midget impingers
Thermometer
Fuel gas line
Center line up
Ice bath
Pressure regulator (if required)
Meter box assembly
Thermometers
Gas petcock
Rate meter
Needle valve
Quick disconnect
Valve
Dry gas meter
Silica gel drying tube
(For air purge)
Pump

40 CFR 60, Method 15 (ABRIDGED)

Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions from Stationary Sources

Introduction

This method uses the principle of gas chromatographic separation and flame photometric detection (FPD).

1.0 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.

2.0 Range and Sensitivity

2.1 Range

Coupled with a gas chromatographic system utilizing a milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppm.

2.2 Sensitivity

The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppm for a 1 mL sample.

3.0 Interferences

3.1 Moisture Condensation

Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the probe, filter box, and connections, and by maintaining the SO_2 scrubber in an ice water bath.

3.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2)

CO and CO_2 have substantial desensitizing effects on the flame photometric detector even after 9:1 dilution. 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 chromatograms should show agreement within the precision limits of Section 4.1.

3.3 Elemental Sulfur

The condensation of sulfur vapor in the sampling system can lead to blockage of the particulate filter. This problem can be minimized by observing the filter for buildup and changing as needed.

3.4 Sulfur Dioxide (SO_2)

Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO_2 scrubber described in Section 5.1.3 will effectively remove SO_2 from the sample.

3.5 Alkali Mist

Alkali mist in the emissions of some control devices may cause a rapid increase in the SO_2 scrubber pH to give low sample recoveries. Replacing the SO_2 scrubber contents after each run will minimize the chances of interference in these cases.

4.0 Precision

4.1 Calibration Precision

A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results that do not vary by more than ± 13 percent from the mean of the three injections.

4.2 Calibration Drift

The calibration drift determined from the mean of three injections made at the beginning and end of any run or series of runs within a 24 hour period shall not exceed ± 5 percent.

5.0 Apparatus

5.1 Sampling

5.1.1 Probe

The probe shall be made of Teflon or Teflon-lined stainless steel and heated to prevent moisture condensation.

5.1.2 Particulate Filter

50 mm Teflon filter holder and a 1-to-2 micron porosity Teflon filter. The filter holder must be maintained in a hot box at a temperature of at least 120°C (248°F).

5.1.3 SO_2 Scrubber

5.1.3.1 Teflon Impingers

Use three 300 mL Teflon segment impingers connected in series with flexible, thick-walled, Teflon tubing. The first two impingers contain 100 mL of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (1/8 in.) I.D. and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0°C.

5.1.3.2 Connections

Connections between the probe, particulate filter, and SO_2 scrubber shall be made of Teflon and be as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber shall be maintained at a temperature of at least 120°C (248° F).

5.1.4 Sample Line

Teflon, no greater than 1.3 cm (1/2 in. I.D.

5.1.5 Sample Pump

The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent.

5.2 Dilution System

The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel. It must be capable of approximately a 9:1 dilution of the sample.

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

Capable of monitoring column oven, detector, and exhaust' temperature ±1°C.

5.3.3 Flow System

Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector

5.3.4.1 Electrometer

Capable of full-scale amplification of linear ranges of 10-1 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.

5.3.4.4 Rotary Gas Valves

Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas.

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.

5.5 Calibration System

The calibration system must contain the following components.

5.5.1 Flow System

To measure air flow over permeation tubes within 2 percent. Each flowmeter shall be calibrated after a complete test series with a wet-test meter.

5.5.2 Constant Temperature Bath

Device capable of maintaining the permeation tubes at the calibration temperature within 0.1°C.

5.5.3 Temperature Gauge

Thermometer or equivalent to monitor bath temperature within 0.1°C.

6.0 Reagents

6.1 Hydrogen

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.

6.6 Citrate Buffer

Dissolve 300 g of potassium citrate and 41 g of anhydrous citric acid in 1 liter of water.

6.7 Sample Line Loss Gas (Optional)

As an alternative, H_2S cylinder gas may be used for the sample line loss test.

7.0 Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem that might occur later and invalidate the entire test.

7.1 Procedures

After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test

Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections.

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.

8.0 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.

8.2 Calibration Procedure

Insert the permeation tubes into the tube chamber. Check the bath temperature to ensure agreement with the calibration temperature of the tubes within ± 0.1°C. Allow 24 hours for the tubes to equilibrate.

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.

8.3 Calibration of Analysis System

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.

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.

9.0 Sampling and Analysis Procedure

9.1 Sampling

Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in Section 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis

9.2.1 Sample Run

A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe or Filter

If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe orifice is clogged with particulate matter.

10.0 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 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.

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 Section 10.2. The calibration drift should not exceed the limits set forth in Section 4.2.

11.0 Calculations

11.1 Determination

Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves.

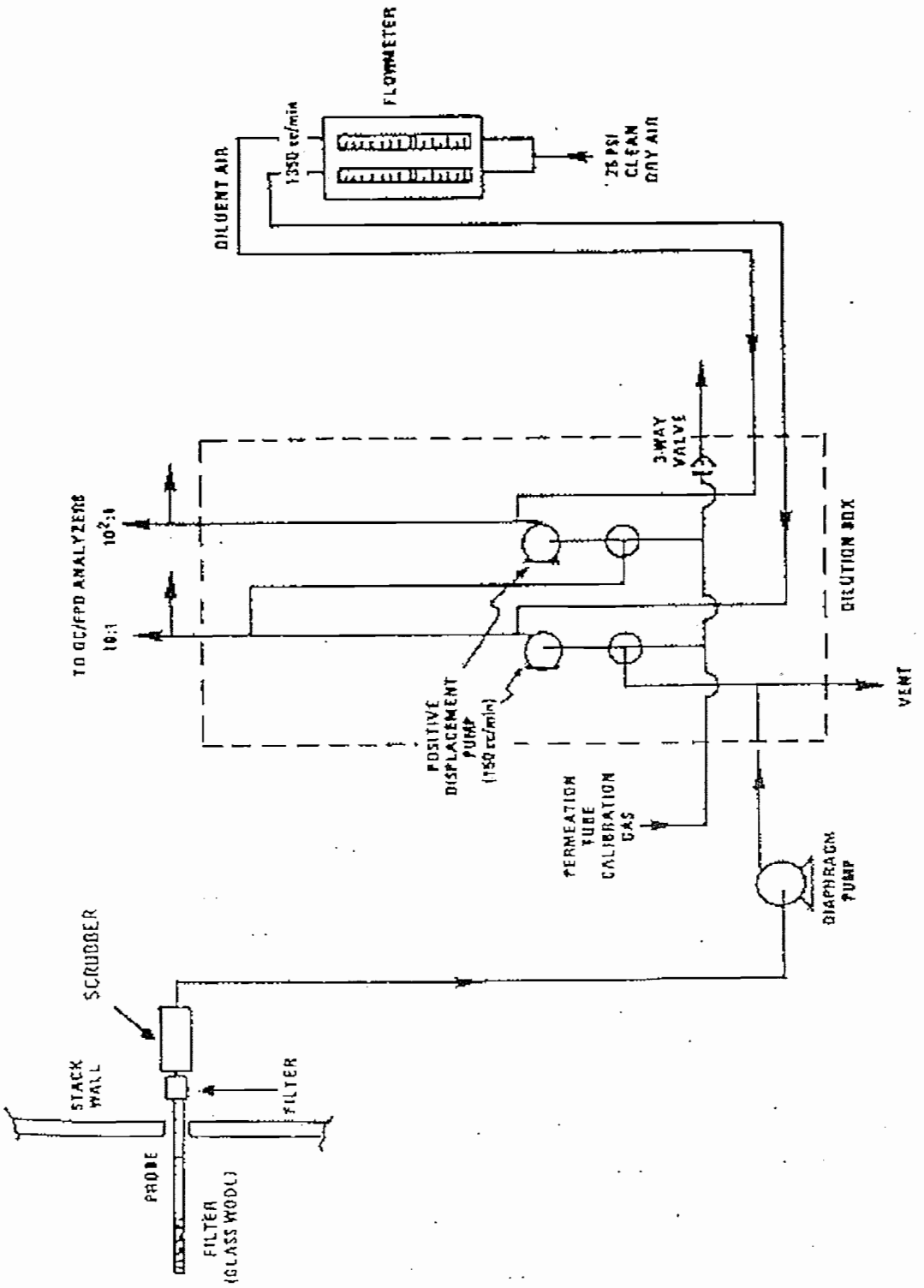
11.2 Calculation of SO_2 Equivalent

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

11.3 Average SO_2 Equivalent

This value is determined using the following equation. Systems that do not remove moisture from the sample but conditions the gas to prevent condensation must correct the average SO_2 equivalent for the fraction of water vapor present.

12.0 Bibliography


FLOWMETER
1350 cc/min
DILUENT AIR
25 PSI
CLEAN
DRY AIR
3-WAY
VALVE
TO GC/FPD ANALYZERS
10^2:1
10:1
DILUTION BOX
VENT
POSITIVE
DISPLACEMENT
PUMP
(150 cc/min)
PERMEATION
TUBE
CALIBRATION
GAS
DIAPHRAGM
PUMP
SCRUBBER
STACK
WALL
FILTER
PROBE
FILTER
(GLASS WOOL)

40 CFR 60, Method 15A (ABRIDGED)

Determination of Total Reduced Sulfur Emissions From Sulfur Recovery Plants in Petroleum Refineries

1.0 Applicability

This method is applicable for the determination of emissions of reduced sulfur compounds from sulfur recovery plants where the emissions are in a reducing atmosphere, such as in Stretford units.

2.0 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

3.0 Principle

An integrated gas sample is extracted from the stack, and combustion air is added to the oxygen (O_2)-deficient gas at a known rate. The reduced sulfur compounds [including carbon disulfide (CS_2), carbonyl sulfide (COS), and hydrogen sulfide (H_2S)] are thermally oxidized to sulfur dioxide (SO_2), which is then collected in hydrogen peroxide as sulfate ion and analyzed according to the Method 6 barium-thorin titration procedure.

4.0 Interferences

Reduced sulfur compounds, other than CS_2, COS, and H_2S, that are present in the emissions will also be oxidized to SO_2, causing a positive bias relative to emission standards that limit only the three compounds listed above.

Calcium and aluminum have been shown to interfere in the Method 6 titration procedure. Since these metals have been identified in particulate matter emissions from Stretford units, a Teflon filter is required to minimize this interference.

Dilution of the hydrogen peroxide (H_2O_2) absorbing solution can potentially reduce collection efficiency, causing a negative bias. When used to sample emissions containing 7 percent moisture or less, the midget impingers have sufficient volume to contain the condensate collected during sampling. Dilution of the H_2O_2 does not affect the collection of SO_2. At higher moisture contents, the potassium citrate-citric acid buffer system used with Method 16A should be used to collect the condensate.

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents

The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2)

Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH)

Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs.

5.2.3 Sulfuric Acid (H_2SO_4)

Rapidly destructive to body tissue.

6.0 Equipment and Supplies

6.1 Sample Collection

The sampling train used in performing this method are discussed below. Modifications to this sampling train are acceptable provided that the system performance check is met.

6.1.1 Probe

6.4 mm (¼-in.) O.D. Teflon tubing sequentially wrapped with heat-resistant fiber strips, a rubberized heating tape (with a

plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or some other suitable temperature-measuring device shall be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored.

6.1.2 Particulate Filter

A 50-mm Teflon filter holder and a 1 to 2-mm porosity Teflon filter.

6.1.3 Combustion Air Delivery System

The rate meter should be selected to measure an air flow rate of 0.5 L/min (0.02 ft^3/min).

6.1.4 Combustion Tube

Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long.

6.1.5 Furnace

Of sufficient size to enclose the combustion tube. The furnace must have a temperature regulator capable of maintaining the temperature at 1100 ± 50°C (2,012 ± 90°F).

6.1.6 Peroxide Impingers

6.1.7 Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as in Method 6, Sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, Section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge and Rate Meter

At least 760 mm Hg (30 in. Hg) gauge and rotameter capable of measuring flow rate to ±5 percent of the selected flow rate and calibrated as in Section 10.2.

6.1.9 Volume Meter. Dry gas meter capable of measuring the sample volume under the particular sampling conditions with an accuracy of 2 percent.

6.1.10 U-tube manometer. To measure the pressure at the exit of the combustion gas dry gas meter.

6.1.11 Sample Recovery and Analysis. Same as Method 6, Sections 6.2 and 6.3, except a 10 mL buret with 0.05 mL graduations is required for titrant volumes of less than 10.0 mL.

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents and standards are required for sample analysis.

7.1.1 Water

Same as Method 6, Section 7.1.1.

7.1.2 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume

Same as Method 6, Section 7.1.3 (40 mL is needed per sample).

7.1.3 Recovery Check Gas

Carbonyl sulfide in nitrogen [100 parts per million by volume (ppmv) or greater, if necessary] in an aluminum cylinder.

7.1.4 Combustion Gas

Air, contained in a gas cylinder equipped with a two-stage regulator.

7.2 Sample Recovery and Analysis

Same as Method 6, Sections 7.2 and 7.3.

8.0 Sample Transport

8.1 Preparation of Sampling Train

For the Method 6 part of the train, measure 20 mL of 3 percent H_2O_2 into the first and second midget impingers. Leave the third midget impinger empty and add silica gel to the fourth impinger.

8.2 Leak Check Procedure

Assemble the sampling train and leak check as described in Method 6, Section 8.2.

8.3 Sample Collection

Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 10 psig. Adjust the combustion air flow rate to 0.5 ± 0.05 L/min (1.1 ± 0.1 ft^3/hr) before injecting combustion air into the sampling train. Then inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve. Carry out these three operations within 15 to 30 seconds to avoid pressurizing the sampling train.

8.4 Sample Recovery

Recover the hydrogen peroxide-containing impingers as detailed in Method 6, Section 8.4.

8.5 System Performance Check

8.5.1 Requirements

A system performance check is done (1) to validate the sampling train components and procedure and (2) to validate a test run.

8.5.2 Procedure

The checks involve sampling a known concentration of COS and comparing the analyzed concentration with the known concentration.

8.5.3 Recovery

The recovery check must be performed in the field before replacing the particulate filter and before cleaning the probe.

9.0 Calibration and Standardization

9.1 Metering System, Temperature Sensors, Barometer, and Barium Perchlorate Solution.

Same as Method 6, Sections 10.1, 10.2, 10.4, and 10.5, respectively.

9.2 Rate Meter

Calibrate with a bubble flow tube.

10.0 Analytical Procedure

10.1 Sample Loss Check and Sample Analysis

Same as Method 6, Sections 11.1.

10.2 Audit Sample Analysis

Same as Method 6, Section 11.3.

11.0 Data Analysis and Calculations

11.1 Nomenclature

11.2 Analytical Range

The lower detectable limit is 0.1 ppmv when sampling at 2 L/min for 3 hours or 0.3 ppmv when sampling at 2 L/min for 1 hour.

11.3 Precision

Relative standard deviations of 2.8 and 6.9 percent have been obtained when sampling a stream with a reduced sulfur compound concentration of 41 ppmv as SO_2 for 1and 3 hours, respectively.

11.4 Bias

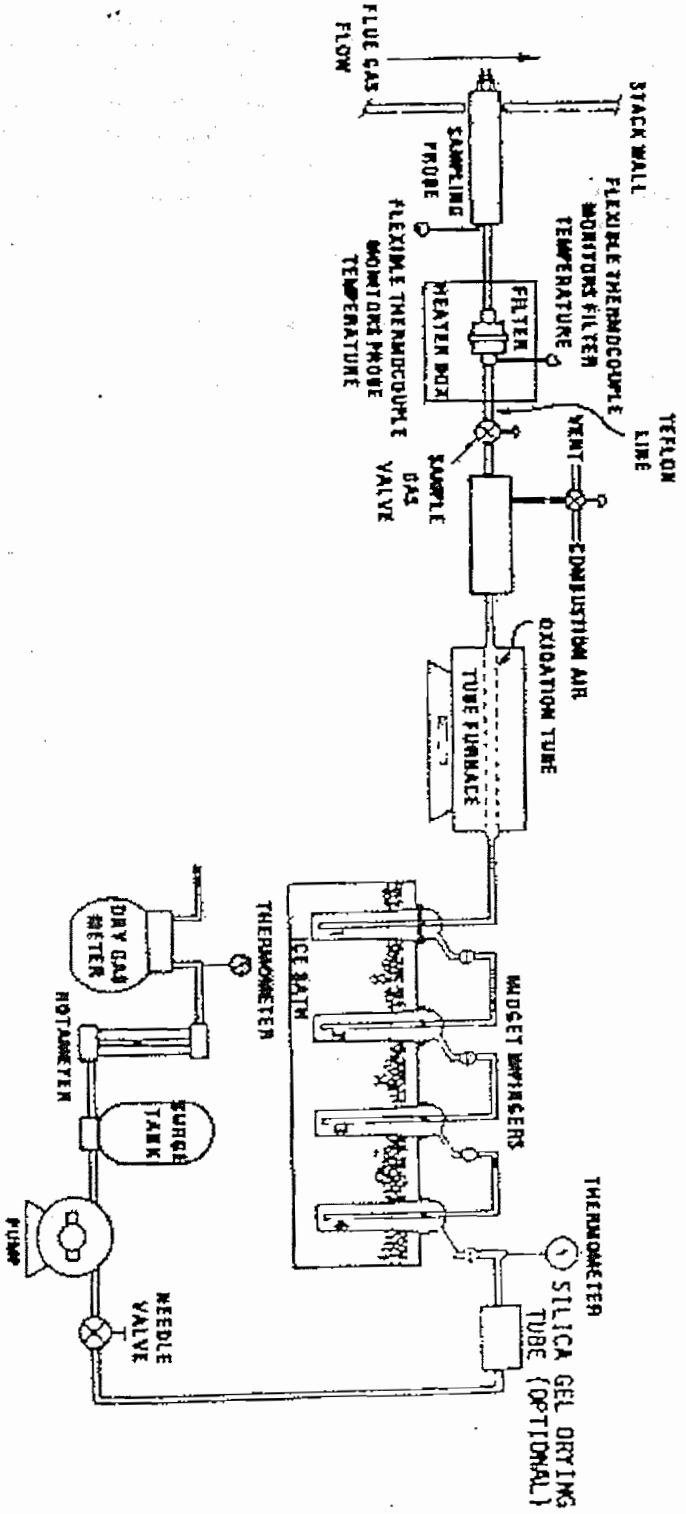
No analytical bias has been identified. However, results obtained with this method are likely to contain a positive bias relative to emission regulations due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the emissions. The magnitude of this bias varies accordingly, and has not been quantified.

12.0 Pollution Prevention

13.0 Waste Management

14.0 References

15.0 Tables, Diagrams, Flowcharts, and Validation Data


FLUE GAS FLOW
STACK WALL
SAMPLING PROBE
FLEXIBLE THERMOCOUPLE MONITORS FILTER TEMPERATURE
FILTER
HEATER BOX
FLEXIBLE THERMOCOUPLE MONITORS PROBE TEMPERATURE
SAMPLE GAS VALVE
VENT
TEFLON LINE
COMBUSTION AIR
OXIDATION TUBE
TUBE FURNACE
ICE BATH
IMPINGERS
THERMOMETER
SILICA GEL DRYING TUBE (OPTIONAL)
THERMOMETER
DRY GAS METER
ROTAMETER
SURGE TANK
PUMP
NEEDLE VALVE

40 CFR 60, Method 16 (ABRIDGED)

Semicontinuous Determination of Sulfur Emissions from Stationary Sources

Introduction

The method described here uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.0 Principle and Application.

1.1 Principle

A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability

This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

2.0 Range and Sensitivity

2.1 Range

The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10 to 0.1 mL sample loop sizes. This eliminates the need for sample dilution in most cases.

2.2 Sensitivity

Using the 10 mL sample size, the minimum detectable concentration is approximately 50 ppb.

3.0 Interferences.

3.1 Moisture

Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences.

3.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2).

CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after dilution.

3.3 Particulate Matter

Particulate matter in gas samples can cause interference by eventual clogging of the analytical system.

3.4 Sulfur Dioxide (SO_2)

Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest.

4.0 Precision and Accuracy

4.1 GC/FPD Calibration Precision

± 5 percent from mean of three injections.

4.2 Calibration Drift

± 5 percent over 24-hours

4.3 System Calibration Accuracy

Correction factor developed through sample transport system

5.0 Apparatus

5.1 Sampling

5.1.1 Probe

Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation.

5.1.2 Particulate Filter

50 mm Teflon filter holder and a 1 to 2 micron porosity Teflon filter. The filter

holder must be maintained in a hot box at a temperature of at least 120°C (248°F).

5.1.3 SO_2 Scrubber

Three 300 mL Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. The first two impingers contain 100 mL of citrate buffer and the third impinger is initially dry.

5.1.4 Sample Line

Teflon, no greater than 1.3 cm I.D..

5.1.5 Sample Pump

The sample pump must be a leak-free Teflon-coated diaphragm type or equivalent.

5.2 Dilution System

The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

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 (2°F).

5.3.2 Temperature Gauge

To monitor column oven, detector, and exhaust temperature 1°C (2°F).

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.

5.3.4.4 Rotary Gas Valves

Multiport Teflon-lined valves equipped with sample loop.

5.4 Gas Chromatogram 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.

5.5 Calibration System

A calibration system, containing the following components.

5.5.1 Tube Chamber

Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.5.2 Flow System

To measure air flow over permeation tubes at ~2 percent.

5.5.3 Constant Temperature Bath.

Device capable of maintaining the permeation tubes at the calibration temperature within 0.1°C (0.2°F).

5.5.4 Temperature Gauge.

Thermometer or equivalent to monitor bath temperature within 1°C (2°F).

6.0 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 (if required)

Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

6.5 6.5 Calibration Gases

Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature.

6.6 Citrate Buffer and Sample Line Loss Gas

Same as Method 15, Sections 7.6 and 7.7.

6.7 Sample Line Loss Gas (Optional)

7.0 Pretest Procedures

7.1 Introduction

7.2 Procedures

After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.2.1 Leak Test

Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections.

7.2.2 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.

8.0 Calibration

Prior to any sampling run, calibrate the system using the following procedures.

8.1 General Considerations

This section outlines steps to be followed for use of the GC/FPD and the dilution system.

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.

8.3 Calibration of Analysis System

Generate a series of three or more known concentrations spanning the linear range of the FPID (approximately 0.5 to 10 ppm for a 1 mL sample) for each of the three major sulfur compounds.

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.

9.0 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

9.2 Analysis

Aliquots of diluted sample are injected into the GC/FPID analyzer for analysis.

9.2.1 Sample Run

A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe or Filter

If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter.

10.0 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.

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.

10.3 Determination of Calibration Drift

Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under Section 10.2. The calibration drift should not exceed the limits set forth in Section 4.2.

11.0 Calculations

11.1 Determination

Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves.

11.2 Calculation of TRS

40 CFR 60, Method 16A (ABRIDGED)

Determination of Total Reduced Sulfur Emissions From Stationary Sources (Impinger Technique)

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Therefore, persons using this method should have a thorough knowledge of the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes

1.2 Applicability

This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at Kraft pulp mills, reduced sulfur compounds (H_2S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Sampling

An integrated gas sample is extracted from the stack. SO_2 is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions

4.0 Interferences

4.1 Reduced Sulfur Compounds

Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate Matter

Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed prior to oxidation.

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents

The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes.

5.2.1 Hydrogen Peroxide (H_2O_2)

5.2.2 Sodium Hydroxide (NaOH)

5.2.3 Sulfuric Acid (H_2SO_4)

5.2.4 Hydrogen Sulfide (H_2S)

6.0 Equipment and Supplies

6.1 Sample Collection

The sampling train and component parts are discussed below.

6.1.1 Probe

Teflon tubing, 6.4 mm (¼ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other

suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe.

6.1.2 Probe Brush

Nylon bristle brush with handle inserted into a 3.2 mm Teflon tubing.

6.1.3 Particulate Filter

50-mm Teflon filter holder and a 1 to 2-µm porosity, Teflon filter.

6.1.4 SO_2 Scrubber

Three, 300 mL Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. The first two impingers contain 100 mL of citrate buffer and the third impinger is initially dry.

6.1.5 Combustion Tube

Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long.

6.1.6 Furnace

A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ± 100°C (1472 ± 180° F).

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer.

Same as Method 6, Sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, Section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge

At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter

Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 L/min (4.2 ft^3/hr).

6.1.10 Volume Meter

Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 L/min (4.2 ft^3/hr) with an accuracy of 2 percent.

6.2 Sample Recovery

Polyethylene Bottles, 250-mL (one per sample).

6.3 Sample Preparation and Analysis

Same as Method 6, Section 6.3, except a 10 mL buret with 0.05 mL graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.1 Sample Collection

The following reagents are required for sample analysis.

7.1.1 Water

Same as in Method 6, Section 7.1.1.

7.1.2 Citrate Buffer

7.1.3 Hydrogen Peroxide, 3 percent

Same as in Method 6, Section 7.1.3 (40 mL is needed per sample).

7.1.4 Recovery Check Gas

Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders.

7.1.5 Combustion Gas

Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons.

7.2 Sample Recovery and Analysis

Same as Method 6, Sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train

For the SO_2 scrubber, measure 100 mL of citrate buffer into the first and second impingers; leave the third impinger empty.

For the Method 6 part of the train, measure 20 mL of 3 percent hydrogen peroxide into the first and second midget impingers. Leave the third midget impinger empty, and place silica gel in the fourth midget impinger.

8.2 Citrate Scrubber Conditioning Procedure

Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 L/min for 10 minutes has been found to be sufficient to obtain equilibrium.

8.3 Sample Collection

Same as in Method 6, Section 8.3, except the sampling rate is 2 L/min (± 10 percent) for 1 or 3 hours.

NOTE: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

8.4 Sample Recovery

Disconnect the impingers. Quantitatively transfer the contents of the midget impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment.

8.5 System Performance Check

8.5.1 Performance Check Schedule

A system performance check is done (1) to validate the sampling train components and procedures (prior to testing) and (2) to validate a test run (after a run). Perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 Performance Check Procedure

The checks involve sampling a known concentration of H_2S and comparing the analyzed concentration with the known concentration.

8.5.3 Sampling and Recovery

Collect 30-minute samples, and analyze in the same manner as the emission samples.

8.5.4 Recovery Check Location

The recovery check must be performed in the field prior to replacing the SO_2 scrubber and particulate filter and before the probe is cleaned.

9.0 Quality Control

10.0 Calibration

Same as Method 6, Section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis

Same as Method 6, Sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-mL aliquot, add 160 mL of 100 percent isopropanol and four drops of thorin.

11.2 Audit Sample Analysis

Same as Method 6, Section 11.3.

11.3 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.0 Nomenclature

13.0 Method Performance

13.1 Analytical Range

The lower detectable limit is 0.1 ppmv SO_2 when sampling at 2 L/min. (4.2 ft^3/hr) for 3 hours or 0.3 ppmv when sampling at 2 L/min. (4.2 ft^3/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision

Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias

13.3.1 Method 16A

No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16

13.3.3 Relative Standard Deviations

Relative standard deviation of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention

15.0 Waste Management

16.0 Alternative Procedures

As an alternative to the procedures specified in Section 7.1.4, the following procedure may be used to verify the H_2S concentration of the recovery check gas.

16.1 Summary

The H_2S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range

The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences

There are no known interferences to this procedure when used to analyze cylinder gases containing H_2S in nitrogen.

16.4 Precision and Bias

Laboratory tests have shown a relative standard deviation of less than 3 percent.

16.5 Equipment and Supplies

16.5.1 Sampling Apparatus

The sampling train component parts are discussed below.

16.5.1.1 Sampling Line

Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve

Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers

Three impingers of approximately 100 mL capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer

Same as Method 11, Sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator

Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter

Calibrated for 100 and 500 mL or two separate bubble meters.

16.5.1.7 Critical Orifice

For volume and rate measurements. The critical orifice may be fabricated according to Section 16.7.3 and must be calibrated as specified in Section 16.12.4.

16.5.1.8 Graduated Cylinder

50 mL size.

16.5.1.9 Volumetric Flask

1 liter size.

16.5.1.10 Volumetric Pipette

15 mL size.

16.5.1.11 Vacuum Gauge

Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch

16.5.2 Sample Recovery and Analysis

16.5.2.1 Erlenmeyer Flasks

125 and 250 mL sizes.

16.5.2.2 Pipettes

Two 10, 20, and 100mL volumetric.

16.5.2.3 Burette

50 mL size.

16.5.2.4 Volumetric Flask

1-liter size.

16.5.2.5 Graduated Cylinder

50 ml size.

16.5.2.6 Wash Bottle

16.5.2.7 Stirring Plate and Bars

16.6 Reagents and Standards

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

16.6.1 Water

Same as Method 11, Section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution

Dissolve 20 g zinc acetate in water and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [$KH(IO_3)_2$] Solution

Standard 0.100 N. Dissolve 3.249 g anhydrous $KH(IO_3)_2$ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ($Na_2S_2O_3$) Solution

Standard 0.1 N. Same as Method 11, Section 7.3.2. Standardize according to Section 16.12.2.

16.6.5 $Na_2S_2O_3$ Solution, Standard 0.01 N

Pipette 100.0 mL of 0.1 N $Na_2S_2O_3$ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N

Same as Method 11, Section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N

Same as in Method 11, Section 7.2.4. Standardize according to Section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight

Add 230 mL concentrated HCl (specific gravity 1.19) to 770 mL water.

16.6.9 Starch Indicator Solution

16.7 Pre-test Procedures

16.7.1 Selection of Gas Sample Volumes

This procedure has been validated for estimating the volume of cylinder gas sample needed when the H_2S concentration is in the range of 5 to 1500 ppmv.

16.7.2 Critical Orifice Flow Rate Selection

A table shows the ranges of sample flow rates that are desirable in order to ensure capture of H_2S in the impinger solution.

16.7.3 Critical Orifice Fabrication

Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1/16 in. X 1/4 in. (0.16 cm X 0.64 cm) reducing fittings to both ends.

16.7.3 Determination of Critical Orifice Approximate Flow Rate

Connect the critical orifice to the sampling

16.7.4 Determination of Approximate Sampling Time

Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in Section 16.7.1.

16.8 Sample Collection.

16.8.1 Connecting Tubing

Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve. Vent the rotameter to an exhaust hood. Plug the open end of the tee.

16.8.2 Place 50 mL of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Record the sampling time.

16.9 Blank Analysis

While the sample is being collected, run a blank.

16.10 Sample Analysis

Sample treatment is similar to the blank treatment.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in Section 16.12.4.

16.12 Calibrations and Standardizations

16.12.1 Rotameter and Barometer

Same as Method 11, Sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N

Standardize the 0.1 N $Na_2S_2O_3$ solution.

16.12.3 Iodine Solution, 0.01 N

Standardize the 0.01 N iodine solution.

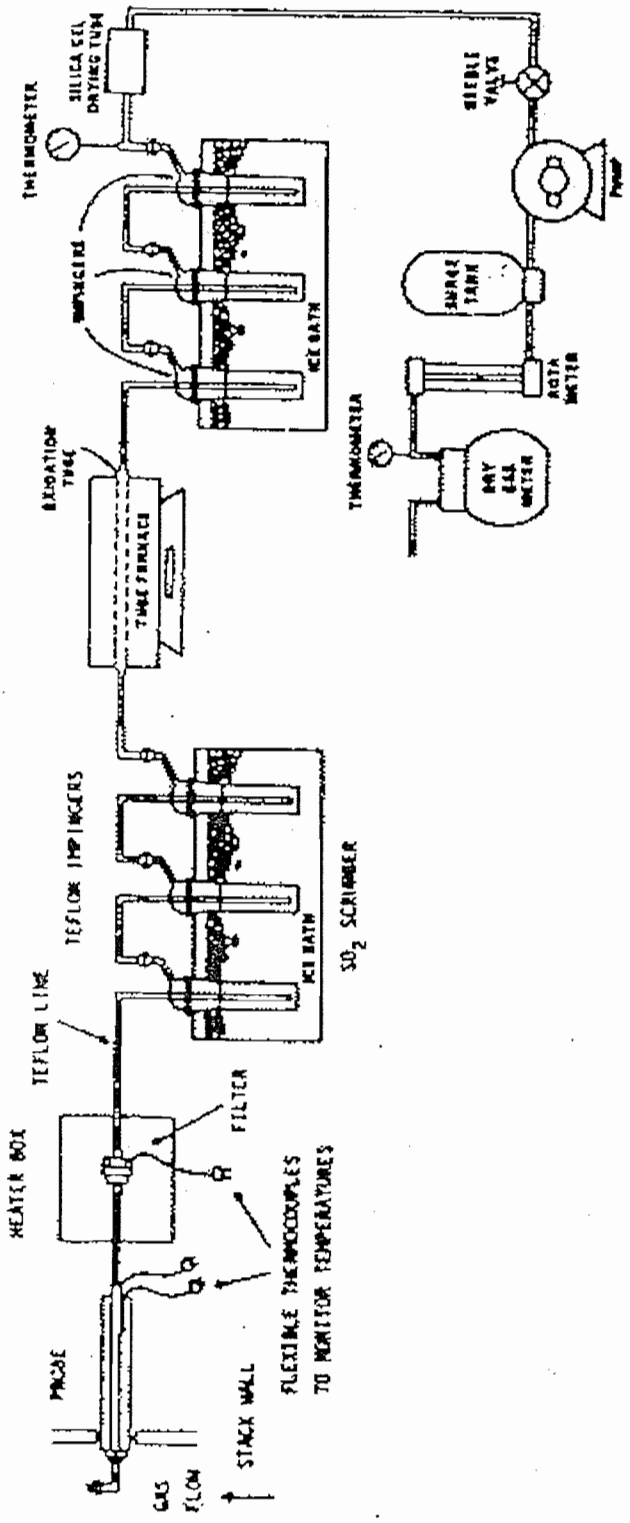
16.12.4 Critical Orifice

Calibrate the critical orifice using the sampling train but without the H_2S cylinder and vent rotameter.

16.13 Calculations.

17.0 References

18.0 Tables, Diagrams, Flowcharts, and Validation Data.


PROBE
STACK WALL
GAS FLOW
HEATER BOX
FILTER
TEFLON LINE
TEFLON IMPINGERS
ICE BATH
SO_2 SCRUBBER
ICE BATH
THERMOMETER
SURGE TANK
THERMOMETER

40 CFR 60, Method 16B (ABRIDGED)

Determination of Total Reduced Sulfur Emissions From Stationary Sources

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes

1.2 Applicability

This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at Kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Sampling

An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions

4.0 Interferences

4.1 Other Reduced Sulfur Compounds

Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferent.

4.2 Particulate Matter

Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber.

4.3 Carbon Monoxide and Carbon Dioxide

Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution.

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hydrogen Sulfide (H_2S)

H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations.

6.0 Equipment and Supplies

6.1 Sample Collection

Modifications to the apparatus are accepted provided the system performance check in Section 8.4.1 is met.

6.1.1 Probe Etc.

Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, Sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump

Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis

6.2.1 Support Equipment

Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, Sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatography Columns

Same as in Method 16, Section 6.2.3.

7.0 Reagents and Standards

Same as in Method 16, Section 7.0, with some exceptions.

7.1 Calibration Gas

SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature.

7.2 Recovery Check Gas.

7.2.1 Hydrogen Sulfide

Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders.

7.2.2 Permeation Device

Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature.

7.3 Combustion Gas

Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures

Same as in Method 15, Section 8.1.

8.2 Sample Collection

Before any source sampling is performed, conduct a system performance check as detailed in Section 8.4.1 to validate the sampling train components and procedures. This test is optional.

8.3 Analysis

Inject aliquots of the sample into the GC/FPD analyzer for analysis.

8.4 Post-Test Procedures

8.4.1 System Performance Check

Same as in Method 16A, Section 8.5.

8.4.2 Calibration Drift

Determination of calibration drift. Same as in Method 15, Section 8.3.2.

9.0 Quality Control

10.0 Calibration

Same as in Method 16, Section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see Section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

12.2 SO_2 Concentration

Determine the concentration of SO_2, C_SO_2, directly from the calibration curves.

12.3 TRS Concentration

12.4 Average TRS Concentration

13.0 Method Performance

13.1 Range and Sensitivity

Coupled with a GC using a 1 mL sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv.

13.2 GC/FPD Calibration and Precision

A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift

The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 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.

13.5 Comparison With Method 16A

Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention

15.0 Waste Management

16.0 References

40 CFR 60, Method 18 (ABRIDGED)

Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

1.0 Principle and Applicability

1.1 Principle

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles.

1.2 Applicability

This method applies to the analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources.

This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

2.0 Range and Sensitivity

2.1 Range

The lower range of this method is determined by the sampling system. The upper limit is governed by GC detector saturation or column overloading.

2.2 Sensitivity

The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one.

3.0 Precision and Accuracy

For this method, the following combined GC/operator values are required.

a. Precision: Duplicate analyses are within 5 percent of their mean value.

b. Accuracy: Analysis results of prepared audit samples are within 10 percent of preparation values.

c. Recovery: After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in Section 7.6. Conduct the appropriate recovery study in Section 7.6 at each sampling point where the method is being applied.

4.0 Interferences

Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

5.0 Pre-survey and Pre-survey Sampling

Perform a pre-survey for each source to be tested.

5.1 Apparatus

This apparatus list also applies to Sections 6 and 7.

5.1.1 Teflon Tubing

Diameter and length are determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

5.1.2 Gas Chromatograph

GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

5.1.3 Pump

Capable of pumping 100 mL/min.

5.1.4 Flow Meters

To measure flow rates.

5.1.5 Regulators

Used on gas cylinders for GC and for cylinder standards.

5.1.6 Recorder

Recorder with linear strip chart is the minimum acceptable type of recorder. Integrator (optional) is recommended.

5.1.7 Syringes

0.5 mL, 1.0 and 10 microliter sizes, calibrated, maximum accuracy (gas tight), for preparing calibration standards.

5.1.8 Tubing Fittings

To plumb GC and gas cylinders.

5.1.9 Septums

For syringe injections.

5.1.10 Glass Jars

If necessary, clean-colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

5.1.11 Soap Film Flow Meter

To determine flow rates.

5.1.12 Tedlar Bags

10 and 50 L capacity, for preparation of standards.

5.1.13 Dry Gas Meter with Temperature and Pressure Gauges

Accurate to ± 2 percent, for preparation of gas standards.

5.1.14 Midget Impinger/Hot Plate Assembly

For preparation of gas standards.

5.1.15 Sample Flasks

For pre-survey samples, must have gas-tight seals.

5.1.16 Adsorption Tubes

If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax®, XAD-2, etc.) for pre-survey samples.

5.1.17 Personnel Sampling Pump

Calibrated, for collecting adsorbent tube pre-survey samples.

5.1.18 Dilution System

Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

5.1.19 Sample Probes

Pyrex or stainless steel, of sufficient length to reach centroid of stack.

5.1.20 Barometer

To measure barometric pressure.

5.2 Reagents

5.2.1 Deionized Distilled Water

5.2.2 Methylene Dichloride

5.2.3 Calibration Gases

A series of standards prepared for every compound of interest.

5.2.4 Organic Compound Solutions

Pure (99.9 percent) gas (pure as can reasonably be obtained), liquid samples of all the organic compounds needed to prepare calibration standards.

5.2.5 Extraction Solvents

For extraction of adsorbent tube samples in preparation for analysis.

5.2.6 Fuel

As recommended by the manufacturer for operation of the GC.

5.2.7 Carrier Gas

Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

5.2.8 Zero Gas

Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

5.3 Sampling

5.3.1 Collection of Samples with Glass Sampling Flasks

Pre-survey samples can be collected in pre-cleaned 250-mL double-ended glass sampling flasks.

Pre-survey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

5.3.1.1 Evacuated Flask Procedure

5.3.1.2 Purged Flask Procedure

5.3.2 Flexible Bag Procedure

5.3.3 Determination of Moisture Content

For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the pre-survey.

5.4 Determination of Static Pressure

Obtain the static pressure from the plant personnel or measurement.

5.5 Collection of Pre-survey Samples with Adsorption Tube

Follow Section 7.4 for pre-survey sampling.

6.0 Analysis Development

6.1 Selection of GC Parameters

6.1.1 Column Choice

6.1.2 Preliminary GC Adjustment

6.1.3 Preparation of Pre-survey Samples

6.1.4 Pre-survey Sample Analysis

6.2 Calibration Standards

6.2.1 Preparation of Standards from High Concentration Cylinder Standards

6.2.2 Preparation of Standards

6.2.2.1 Gas Injection Technique

6.2.2.2 Liquid Injection Technique

6.3 Preparation of Calibration Curves

6.4 Relative Response Factors

6.5 Quality Assurance for Laboratory Procedures

7.0 Final Sampling and Analysis Procedure

Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Sections 7.1, 7.2, 7.3, or 7.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

7.1 Integrated Bag Sampling and Analysis

7.1.1 Evacuated Container Sampling Procedure

In this procedure, the bags are filled by evacuating the rigid air-tight containers that hold the bags.

7.1.1.1 Apparatus

7.1.1.1.1 Probe

Stainless steel, Pyrex glass, or Teflon tubing probe.

7.1.1.1.2 Quick Connects

Male (2) and female (2) of stainless steel construction.

7.1.1.1.3 Needle Valve

To control gas flow.

7.1.1.1.4 Pump

Leak-free Teflon-coated diaphragm type pump or equivalent.

7.1.1.1.5 Charcoal Adsorption Tube

Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

7.1.1.1.6 Flow Meter

0 to 500 mL flow range; with manufacturer's calibration curve.

7.1.1.2 Sampling Procedure

To obtain a sample, assemble the sample train. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack, or at a point no closer to the walls than 1 m and start the pump with the needle valve adjusted to yield a flow of 0.5 L/min. 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. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the field test

data sheet. Protect the Tedlar bag and its container from sunlight.

7.1.2 Direct Pump Sampling Procedure

Follow Section 7.1.1, except place the pump and needle valve between the probe and the bag.

7.1.3 Explosion Risk Area Bag Sampling Procedure

Follow Section 7.1.1 except replace the pump with another evacuated can.

7.1.4 Other Modified Bag Sampling Procedures

7.1.5 Analysis of Bag Samples

7.1.5.1 Apparatus (Same as Section 5)

7.1.5.2 Procedure

7.1.6 Determination of Bag Water Vapor Content

7.1.7 Quality Assurance

7.1.8 Emission Calculations

From the average calibration curve, select the value of C_s, that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample.

7.2 Direct Interface Sampling and Analysis Procedure

The direct interface procedure can be used provided that (1) the moisture content of the gas does not interfere with the analysis procedure, (2) the physical requirements of the equipment can be met at the site, and (3) the source gas concentration is low enough that detector saturation is not a problem.

7.2.1 Apparatus

7.2.1.1 Probe

Constructed of stainless steel, Pyrex glass, or Teflon tubing.

7.2.1.2 Sample Lines

6.4 mm O.D. Teflon lines, heat-traced to prevent condensation of material.

7.2.1.3 Quick Connects

Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

7.2.1.4 Thermocouple Readout Device

Potentiometer or digital thermometer, to measure source temperature and probe temperature.

7.2.1.5 Heated Gas Sampling Valve

Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

7.2.1.6 Needle Valve

To control gas sampling rate from the source.

7.2.1.7 Pump

Leak-free Teflon-coated diaphragm-type plump or equivalent, capable of at least 1 L/min. sampling rate.

7.2.1.8 Flow Meter

Of suitable range to measure sampling rate.

7.2.1.9 Charcoal Adsorber

To adsorb organic vapor collected from the source to prevent exposure of personnel to source gas.

7.2.1.10 Gas Cylinders

Carrier gas (helium or nitrogen), and oxygen and hydrogen for a flame ionization detector (FID) if one is used.

7.2.1.11 Gas Chromatograph

Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

7.2.1.12 Recorder/Integrator

To record results.

7.2.2 Procedure

[Refer to the full text of the CFR for Method 18.]

7.2.3 Determination of Stack Gas Moisture Content

Use Method 4 to measure the stack gas moisture content.

7.2.4 Quality Assurance

Same as Section 7.1.7.

7.2.5 Emission Calculations

Same as Section 7.1.8.

7.3 Dilution Interface Sampling and Analysis Procedure

Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector.

7.3.1 Apparatus

The equipment required in addition to that specified for the direct interface system is as follows:

7.3.1.1 Sample Pump

Leak-free Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 L/min.

7.3.1.2 Dilution Pumps

Two Model A-150 Komhyr Teflon positive-displacement-type delivering 150 cc/min.

7.3.1.3 Valves

Two Teflon three-way valves, suitable for connecting to 6.4-mm O.D. Teflon tubing.

7.3.1.4 Flow Meters

Two, for measurement of diluent gas, expected delivery flow rate to be 1,350 cc/min.

7.3.1.5 Diluent Gas with Cylinders and Regulators

7.3.1.6 Heated Box

Suitable for being heated to 120°C, to contain the three pumps, three-way valves, and associated connections.

7.3.2 Procedure

[Refer to the full text of the CFR for Method 18.]

7.3.3 Determination of Stack Gas Moisture Content

Same as Section 7.2.3.

7.3.4 Quality Assurance

Same as Section 7.2.4.

7.3.5 Emission Calculations

Same as Section 7.2.5, with the dilution factor applied.

7.4 Adsorption Tube Procedure (Alternative Procedure)

It is suggested that the tester refer to the National Institute of Occupational Safety and Health (NIOSH) method for the particular organics to be sampled.

7.4.1 Additional Apparatus

In addition to the equipment listed in the NIOSH method for the particular organic(s) to be sampled, the following items (or equivalent) are suggested.

7.4.1.1 Probe (Optional)

Borosilicate glass or stainless steel, approximately 6 mm I.D.

7.4.1.2 Flexible Tubing

To connect probe to adsorption tubes.

7.4.1.3 Leak-free Sample Pump

Flow controlled, constant-rate pump, with a set of limiting (sonic) orifices to provide pumping rates from approximately 10 to 100 cc/min.

7.4.1.4 Bubble-Tube Flow Meter

Volume accuracy within ± 1 percent, to calibrate pump.

7.4.1.5 Stopwatch

To time sampling and pump rate calibration.

7.4.1.6 Adsorption Tubes

Similar to ones specified by NIOSH, except the amounts of adsorbent per primary backup sections are 800/200 mg for charcoal tubes and 1040/260 mg for silica gel tubes.

7.4.1.7 Barometer

Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

7.4.1.8 Rotameter

0 to 100 cc/min, to detect changes inflow rate during sampling.

7.4.2 Sampling and Analysis

It is suggested that the tester follow the sampling and analysis portion of the respective NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble-tube flow meter before sampling.

7.4.3 Standards and Calibration

The standards can be prepared according to the respective NIOSH method. Use a minimum of three different standards.

7.4.4 Quality Assurance

7.4.4.1 Determine the recovery efficiency of the pollutants of interest according to Section 7.6

7.4.4.2 Determination of Sample Collection Efficiency

7.4.4.3 Analysis Audit

7.4.4.4 Pump Leak Checks and Volume Flow Rate Checks

Perform both of these checks immediately after sampling with all sampling train components in place.

7.4.4.5 Calculations

All calculations can be performed according to the respective NIOSH method. Correct all sample volumes to standard conditions.

7.5 Reporting of Results

7.6 Recovery Study

7.6.1 Recovery Study for Direct Interface or Dilution Interface Sampling

If the procedures in Section 7.2 or 7.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in Section 7.2.2 or 7.3.2, as appropriate.

7.6.2 Recovery Study for Bag Sampling

Follow the procedures for bag sampling and analysis in Section 7.1.

7.6.3 Recovery Study for Adsorption Tube Sampling

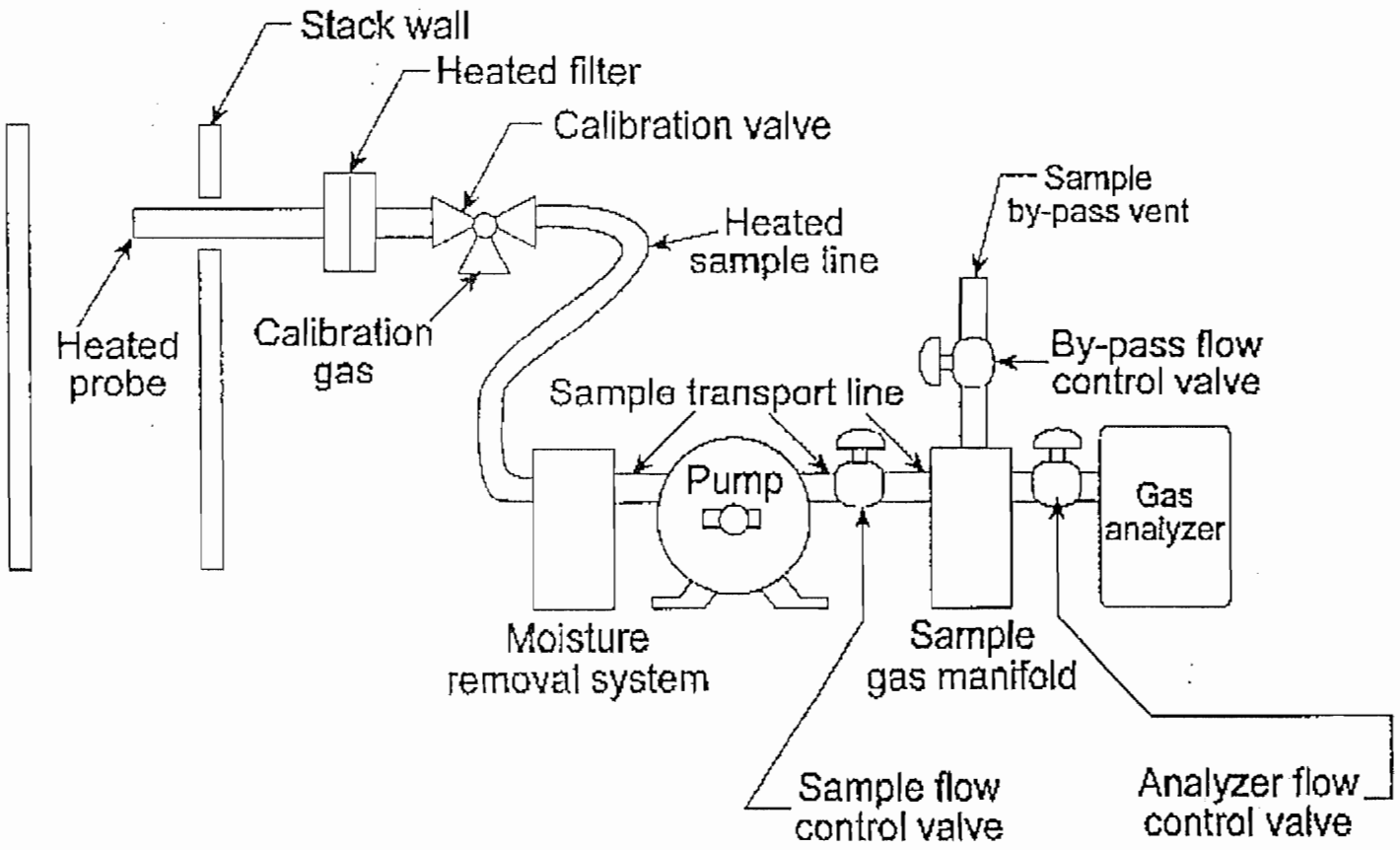
If following the adsorption tube procedure in Section 7.4, conduct a recovery study of the compounds of interest during the actual field test.

7.6.3.1 Repeat Procedure

Repeat the procedure in Section 7.6.3 twice more, for a total of three runs.

8.0 Bibliography

Measurement System Schematic



40 CFR 60, Method 20 (ABRIDGED)

Determination of Nitrogen Oxides, Sulfur Dioxide, and Turbines Oxygen Emissions from Stationary Gas Sources

1.0 Applicability And Principle

1.1 Applicability. This method is applicable for the determination of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and oxygen (O_2) emissions from stationary gas turbines. For the NO_x and O_2 determinations, this method includes: (1) measurement system design criteria, (2) analyzer performance specifications and performance test procedures; and (3) procedures for emission testing.

1.2 Principle. A gas sample in continuously extracted from the exhaust stream of a stationary gas turbine; a portion of the sample stream is conveyed to instrumental analyzers for determination of NO_x and O_2 content. During each NO_x and O_2 determination, a separate measurement of SO_2 emissions is made, using Method 6, or its equivalent. The O_2 determination is used to adjust the NO_x and SO_2 concentrations to a reference condition.

2.0 Definitions

2.1 Measurement System. The total equipment required for the determination of a gas concentration or a gas emission rate.

2.1.1 Sample Interface. That portion of a system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzers from the effects of the stack effluent.

2.1.2 NO_x Analyzer. That portion of the system that senses NO_x and generates an output proportional to the gas concentration.

2.1.3 O_2 Analyzer. That portion of the system that senses O_2 and generates an output proportional to the gas concentration.

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations.

2.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.4 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

2.5 Zero Drift. the difference in the measurement system output readings from zero after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input concentration at the time of the measurements was zero.

2.6 Calibration Drift. The difference in the measurement system output readings from the known concentration of the calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input at the time of the measurements was a high-level value.

2.7 Response Time. The amount of time required for the continuous monitoring system to display 95 percent of a step change in pollutant concentration.

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

3.0 Measurement System Performance Specifications

3.1 NO_2 to NO Converter. Greater than 90 percent conversion efficiency of NO_2 to NO.

3.2 Interference Response. Less than 2 percent of span value.

3.3 Response Time. No greater than 3 seconds.

3.4 Zero Drift. Less than 2 percent of span value over the period of each test run.

3.5 Calibration Drift. Less than 2 percent of span value over the period of each test run.

4.0 Apparatus And Reagent

4.1 Measurement System. Use any measurement system for NO_x and O_2 that is expected to meet the specifications in this method. The essential components of the measurement system are described below:

4.1.1 Probe. Heated stainless steel, or equivalent, open-ended, straight tube of sufficient length to traverse the sample points.

4.1.2 Sample Line. Heated (>95°C) stainless steel or Teflon tubing to transport the sample gas to the sample conditioners and analyzers.

4.1.3 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the sample conditioners and to the analyzers.

4.1.4 NO_2 to NO Converter. That portion of the system that converts NO_2 in the sample gas to NO.

4.1.5 Moisture Removal Trap. A refrigerator-type condenser or other type device designed to continuously remove condensate from the sample gas while maintaining minimal contact between any condensate and the sample gas.

4.1.6 Particulate Filter. An in-stack or an out-of-stack glass fiber filter, of the type specified in Method 5.

4.1.7 Sample Pump. A nonreactive leak-free sample pump to pull the sample gas through the system at a flow rate sufficient to minimize transport delay.

4.1.8 Sample Gas Manifold. A sample gas manifold to divert portions of the sample gas stream to the analyzers.

4.1.9 Diluent Gas Analyzer. An analyzer to determine the percent O_2 or CO_2 concentration of the sample gas stream.

4.1.10 Nitrogen Oxides Analyzer. An analyzer to determine the ppm NO_x concentration in the sample gas stream.

4.1.11 Output. A strip-chart recorder, analog computer, or digital recorder for recording measurement data.

4.2 SO_2 Analysis. Method 6 apparatus and reagents.

4.3 NO_x Calibration Gases. The calibration gases for the NO_x analyzer shall be NO in N_2. Use four calibration gas mixtures as specified below.

4.3.1 High-level Gas. A gas concentration that is equivalent to 80 to 90 percent of the span value.

4.3.2 Mid-level Gas. A gas concentration that is equivalent to 45 to 55 percent of the span value.

4.3.3 Low-level Gas. A gas concentration that is equivalent to 20 to 30 percent of the span value.

4.3.4 Zero Gas. A gas concentration of less than 0.25 percent of the span value. Ambient air may be used for the NO_x zero gas.

4.4 Diluent Calibration Gases. Use purified air at 20.9 percent O_2 as the high-level O_2 gas.

5.0 Measurement System Performance Test Procedures

Perform the following procedures before measurement of emissions (Section 6) and only once for each test program, i.e., the series of all test runs for a given gas turbine engine.

5.1 Calibration Gas Checks. There are two alternatives for checking gases.

(a) The first is to use calibration gases that are documented traceable to National Bureau of Standards Reference Materials.

(b) The second alternative is to use calibration gases not prepared according to the protocol. If this alternative is chosen, within 1 month prior to the emission test, analyze each of the calibration gas mixtures in triplicate using Method 7 for NO_x and use Method 3 for O_2 or CO_2. Record the results on a data sheet.

5.2 Measurement System Preparation. Before the emission test, assemble the measurement system following the manufacturer's written instructions in preparing and operating the NO_2 to NO converter, the NO_x analyzer, the O_2 analyzer, and other components.

5.3 Calibration Check. Conduct the calibration checks for both the NO_2 and the diluent analyzers as follows:

5.3.1 After the measurement system has been prepared for use (Section 5.2), introduce zero gases and the mid-level calibration gases; set the analyzer output responses to the appropriate levels. Then introduce each of the remainder of the calibration gases described in Section 4.3 or 4.4, one at a time, to the measurement system. Record the responses.

5.3.2 If the linear curve determined from the zero and mid-level calibration gas responses does not predict the actual response of the low-level (not applicable for the diluent

analyzer) and high-level gases within 2 percent of the span value, the calibration shall be considered invalid. Take corrective measures on the measurement system before proceeding with the test.

5.4 Interference Response.

5.4.1 Introduce the gaseous components into the measurement system separately, or as gas mixtures. Determine the total interference output response of the system to these components in concentration units; record the values. If the sum of the interference responses of the test gases for either the NO_x or diluent analyzers is greater than 2 percent of the applicable span value, take corrective measures on the measurement system.

5.4.2 Conduct an interference response test of each analyzer before its initial use in the field.

5.4.3 In lieu of conducting the interference response test, instrument vendor data, which demonstrate that for the test gases, the interference performance specification is not exceeded, are acceptable.

5.5 Response Time. Determine response time. Record the response time data. Conduct a response time test before the initial field use of the measurement system, and repeat if changes are made in the measurement system.

5.6 NO_2 to NO Conversion Efficiency.

5.6.1 Add gas from the mid-level NO in N_2 calibration gas cylinder to a clean, evacuated, leak-tight Tedlar bag. Dilute this gas approximately 1:1 with 20.9 percent O_2, purified air. Immediately attach the bag outlet to the calibration valve assembly and begin operation of the sampling system.

5.6.2 Alternatively, the NO_2 to NO converter check described in title 40, Part 86: Certification and Test Procedures for Heavy-duty Engines for 1979 and Later Model Years, may be used.

6.0 Emission Measurement Test Procedure

6.1 Preliminaries.

6.1.1 Selection of a Sampling Site. Select a sampling site as close as practical to the exhaust of the turbine.

6.1.2 A preliminary O_2 or CO_2 traverse is made for the purpose of selecting sampling points of low O_2 values or high CO_2 concentrations as appropriate for the measurement system.

6.1.2.1 Minimum Number of Points. Select a minimum number of points as follows: (1) Eight, for stacks having cross-sectional areas less than 1.5 m^2 (16.1 ft^2); (2) eight plus one additional sample point for each 0.2 m^2 (2.2 ft^2) of areas, for stacks of 1.5 m^2 to 10.0 m^2 (16.1 to 107.6 ft^2) in cross sectional area; and (3) 49 sample points (48 for circular stacks) for stacks greater than 10.0 m^2 (107.6 ft^2) in cross-sectional area.

6.1.2.2 Cross-sectional Layout and Location of Traverse Points. After the number of traverse points for the preliminary diluent sampling has been determined, use Method 1 to locate the traverse points.

6.1.2.3 Preliminary Diluent Measurement. While the gas turbine is operating at the lowest percent of peak load, conduct a preliminary diluent measurement.

6.1.2.4 Selection of Emission Test Sampling Points. Select the eight sampling points at which the lowest O_2 concentrations or highest CO_2 concentrations were obtained.

6.2 NO_x and Diluent Measurement. This test is to be conducted at each of the specified load conditions. Three test runs at each load condition constitute a complete test.

6.2.1 At the beginning of each NO_x test run and, as applicable, during the run, record turbine data.

6.2.2 Position the probe at the first point determined in the preceding section and begin sampling. The minimum sampling time at each point shall be at least 1 minute plus the average system response time.

6.2.3 After sampling the last point, conclude the test run by recording the final turbine operating parameters and by determining the zero and calibration drift.

6.3 SO_2 Measurement.

6.3.1 This test is conducted only at the 100 percent peak load condition. Determine SO_2 using Method 6.

6.3.2 If the applicable regulation allows fuel sampling and analysis for fuel sulfur content to demonstrate compliance with a sulfur

emission unit, emission sampling with Method 6 is not required.

7.0 Emission Calculations

7.1 Moisture Correction. Measurement data used in most of these calculations must be on a dry basis.

7.2 CO_2 Correction Factor. If pollutant concentrations are to be corrected to 15 percent O_2, and CO_2 concentration is measured in lieu of O_2 concentration measurement, a CO_2 correction factor is needed. Calculate the CO_2 correction factor.

7.2.1 Calculate the fuel-specific F_0 value for the fuel burned during the test using values obtained from Method 19, Section 5.2.

7.2.2 Calculate the CO_2 correction factor for correcting measurement data to 15 percent oxygen.

7.3 Correction of Pollutant Concentrations to 15 percent O_2. Calculate the NO_x and SO_2 gas concentrations adjusted to 15 percent O_2.

7.3.1 Correction of Pollutant Concentration Using O_2 Concentration. Calculate the O_2 corrected pollutant concentration.

7.3.2 Correction of Pollutant Concentration Using CO_2 Concentration. Calculate the CO_2 corrected pollutant concentration.

7.3.2.1 Average Adjusted NO_x Concentration. Calculate the average adjusted NO_x concentration by summing the adjusted values for each sample point and dividing by the number of points for each run.

7.3.2.2 NO_x and SO_2 Emission Rate Calculations. The emission rates for NO_x and SO_2 in units of pollutant mass per quantity of heat input can be calculated using the pollutant and diluent concentrations and fuel-specific F-factors based on the fuel combustion characteristics. The measured concentrations of pollutant in units of parts per million by volume (ppm) must be converted to mass per unit volume concentration units for these calculations.

7.3.2.3 Calculation of Emission Rate Using Oxygen Correction. Both the O_2 concentration and the pollutant concentration must be on a dry basis. Calculate the pollutant emission rate.

7.3.2.4 Calculation of Emission Rate Using Carbon Dioxide Correction. The CO_2 concentration and the pollutant concentration may be on either a dry basis or a wet basis, but both concentrations must be on the same basis for the calculations. Calculate the pollutant emission rate.

8.0 Bibliography

40 CFR 60, Method 23 (ABRIDGED)

Determination of Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans from Stationary Sources

1.0 Principle and Applicability

1.1 Principle

A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

1.2 Applicability

This method is applicable to the determination of PCDD's and PCDF's from stationary sources.

2.0 Apparatus

2.1 Sampling

The train is identical to that described in Section 2.1 of Method 5 with the following additions:

2.1.1 Nozzle

The nozzle shall be made of nickel, nickel plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines

The sample transfer lines, if needed, shall be heat-traced, heavy-walled TFE (1/2 in. O.D. with 1/8 in. wall) with connecting fittings that are capable of forming leak free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120°C.

2.2 Filter Support

Teflon or Teflon-coated wire.

2.2.1 Condenser

Glass, coil type with compatible fittings.

2.2.2 Water Bath

Thermostatically controlled to maintain the gas temperature exiting the condenser at <20°C (68°F).

2.2.3 Adsorbent Module

Glass container to hold the solid adsorbent.

2.3 Sample Recovery

2.3.1 Fitting Caps

Ground glass, Teflon tape, or aluminum foil to cap off the sample exposed sections of the train.

2.3.2 Wash Bottles

Teflon, 500 mL

2.3.3 Probe Liner, Probe Nozzle, and Filter Holder Brushes

Inert bristle brushes with pre-cleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe.

2.3.4 Filter Storage Container

Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.3.5 Balance

Triple beam.

2.3.6 Aluminum Foil

Heavy duty, hexane-rinsed.

2.3.7 Metal Storage Container

Air tight container to store silica gel.

2.3.8 Graduated Cylinder

Glass, 250 mL with 2 mL graduation.

2.3.9 Glass Sample Storage Container

Amber glass bottle for sample glassware washes, 500 or 1000 mL, with leak-free Teflon-lined caps.

2.4 Analysis

2.4.1 Sample Container

2.4.2 Test Tube

2.4.3 Soxhlet Extraction Apparatus

2.4.4 Extraction Thimble

2.4.5 Pasteur Pipettes

2.4.6 Reacti-vials

2.4.7 Rotary Evaporator

2.4.8 Nitrogen Evaporative Concentrator

2.4.9 Separatory Funnels

2.4.10 Gas Chromatograph

2.4.10.1 Oven

2.4.10.2 Temperature Gauge

2.4.10.3 Flow System

2.4.10.4 Capillary Columns

2.4.11 Mass Spectrometer

2.4.12 Data System

2.4.13 Analytical Balance

3.0 Reagents

3.1 Sampling

3.1.1 Filters

Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 298671 (Re-approved 1978).

3.1.1.1 Pre-cleaning

All filters shall be cleaned before their initial use.

3.1.2 Adsorbent Resin

Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 CleaningProcedure

This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2.

3.1.2.1.1 Drying Column

Pyrex pipe, 10.2 cm I.D. by 0.6 m long, with suitable retainers.

3.1.2.1.2 Procedure

The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic. contaminants.

3.1.2.2 Quality Control *Check*

The adsorbent must be checked for residual toluene.

3.1.2.2.1 Extraction

Weigh 1.0 g sample of dried resin into a small vial, add 3 mL of toluene, cap the vial, and shake it well.

3.1.2.2.2 Analysis

3.1.2.3 Storage

3.1.3 Glass Wool

Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110°C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water

Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel

Indicating type, 6 to 16 mesh.

3.1.6 Chromic Acid Cleaning Solution

Dissolve 20 g of sodium dichromate in 15 mL of water, and then carefully add 400 mL of concentrated sulfuric acid.

3.2 SampleRecovery

3.2.1 Acetone

Pesticide quality.

3.2.2 Methylene Chloride

Pesticide quality.

3.2.3 Toluene Pesticide quality.

3.3 Analysis

3.3.1 Potassium Hydroxide

3.3.2 Sodium Sulfate

3.3.3 Sulfuric Acid

3.3.4 Sodium Hydroxide

3.3.5 Hexane

3.3.6 Methylene Chloride

3.3.7 Benzene

3.3.8 Ethyl Acetate

3.3.9 Methanol

3.3.10 Toluene

3.3.11 Nonane

3.3.12 Cyclohexane

3.3.13 Basic Alumina

3.3.14 Silica Gel

3.3.15 Silica Gel Impregnated with Sulfuric Acid

3.3.16 Silica Gel Impregnated with Sodium Hydroxide

3.3.17 Carbon/Celite

3.3.18 Nitrogen

3.3.19 Hydrogen

3.3.20 Internal Standard Solution

3.3.21 Surrogate Standard Solution

3.3.22 Recovery Standard Solution

4.0 Procedure

4.1 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

4.1.1.1 Cleaning Glassware

All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples."

4.1.1.2 Adsorbent Trap

The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 mL of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train

It is suggested that all components be maintained according to the procedure described in APTD-0576.

4.1.1.4 Silica Gel

Weigh several 200 to 300 g portions of silica gel in an airtight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container.

4.1.1.5 Filter

Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations

Same as Section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train

4.1.3.1 Seal Openings

During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

4.1.3.2 Charging Impingers

Place approximately 100 mL of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately

200 to 300 g of pre-weighed silica gel from its container to the fifth impinger.

4.1.3.3 Silica Gel

Place the silica gel container in a clean place for later use in the sample recovery.

4.1.3.4 Assemble

Assemble the train.

4.1.3.5 Operation

Turn on the adsorbent module and condenser coil re-circulating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50°C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak Check Procedure

Same as Method 5, Section 4.1.4.

4.1.5 Sample Train Operation

Same as Method 5, Section 4.1.5.

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. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1

Either seal the filter holder or carefully remove the Filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter.

4.2.2 Adsorbent Module

Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No.2

Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone (if used first) by brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 min. each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line.

Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3

Repeat the methylene chloride rinsing described in Section 4.2.3 using toluene as the rinse solvent.

Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

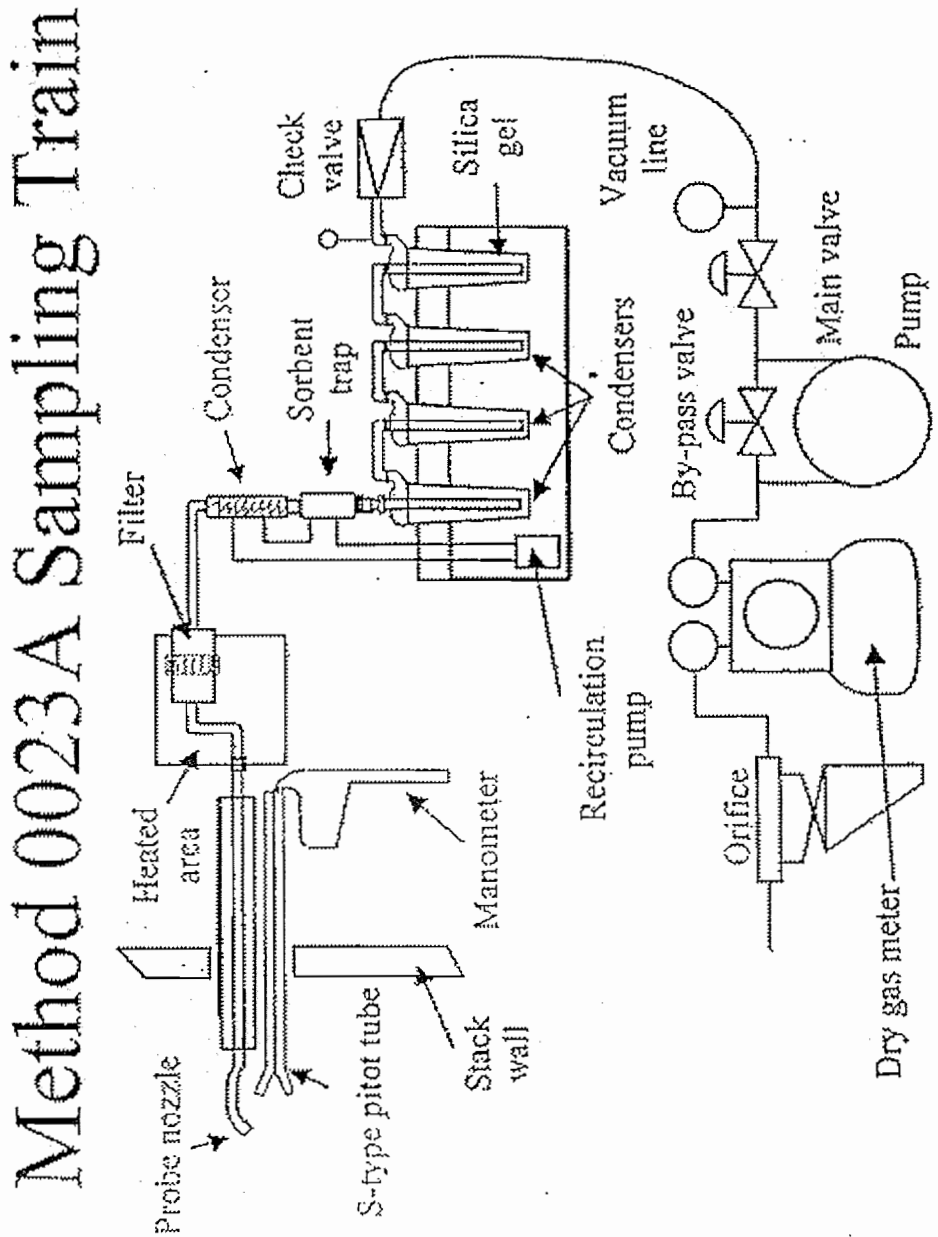
4.2.5 Impinger Water

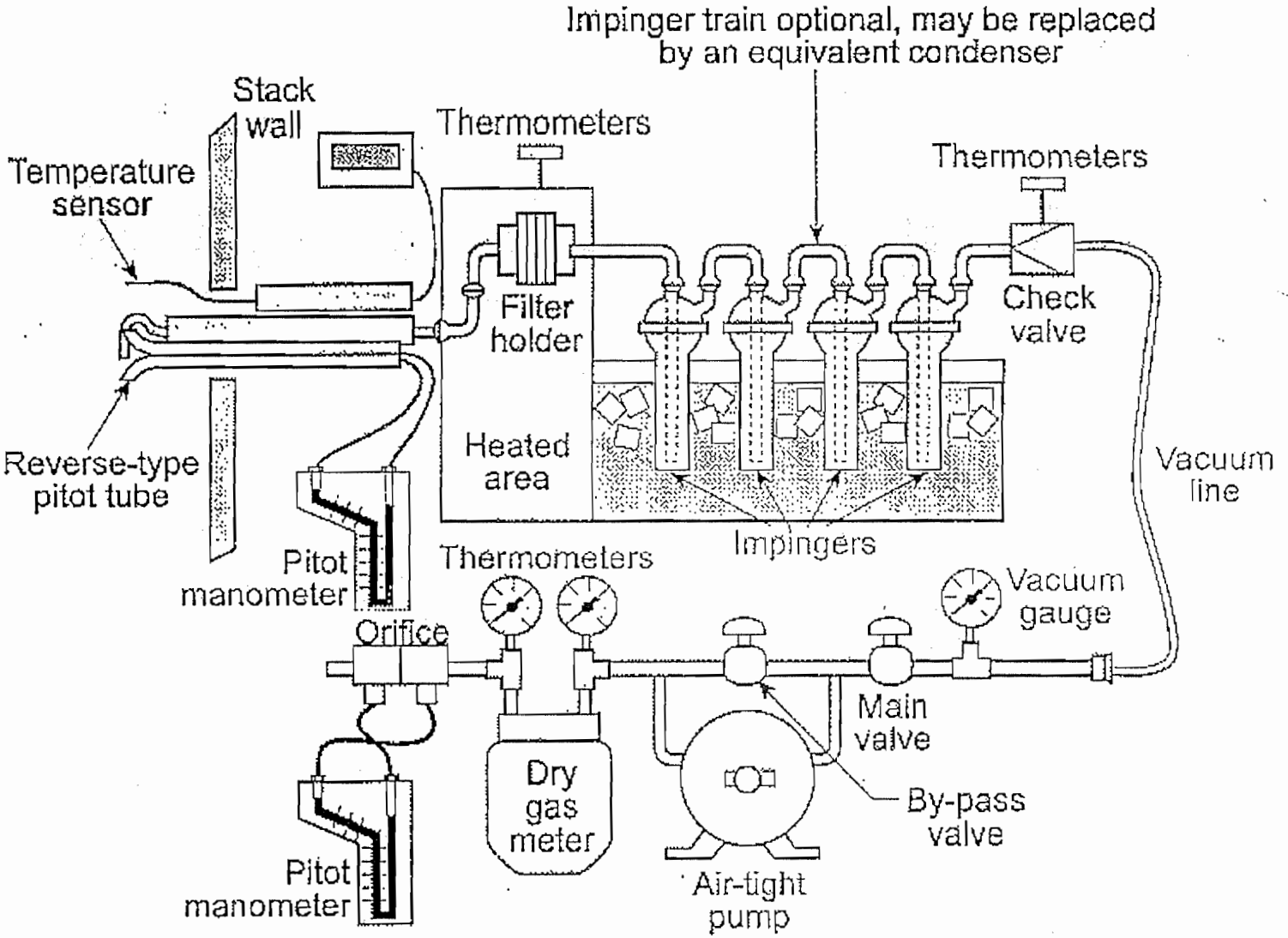
Measure the liquid in the first three impingers to within 1 mL by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

9.9 Total Concentration of PCDDs and PCDFs in the Sample

Any PCDDs or PCDFs that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDDs and PCDFs in the sample.

10.0 Bibliography


Method 0023A Sampling Train
Probe nozzle
Heated area
Filter
Condenser
Sorbent trap
Check valve
Silica gel
Vacuum line
Condensers
By-pass valve
Main valve
Pump
Recirculation pump
Manometer
S-type pitot tube
Stack wall
Orifice
Dry gas meter


Impinger train optional, may be replaced by an equivalent condenser
Stack wall
Thermometers
Thermometers
Temperature sensor
Filter holder
Check valve
Heated area
Vacuum line
Reverse-type pitot tube
Impingers
Pitot manometer
Thermometers
Vacuum gauge
Orifice
Main valve
Dry gas meter
By-pass valve
Pitot manometer
Air-tight pump

40 CFR 60, Method 25 (ABRIDGED)

Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1.0 Applicability and Principle

1.1 Principle

An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the total gaseous nonmethane organics (TGNMO) are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results.

1.2 Applicability

This method applies to the measurement of volatile organic compounds (VOC) as TGNMO as carbon in source emissions. Organic particulate matter will interfere with the analysis and, therefore, a particulate filter is required. The minimum detectable for the method is 50 ppm as carbon.

When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample.

This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer maybe appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured.

In situations where a qualitative or quantitative analysis of an effluent stream is desired or required, a gas chromatographic (GC) FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

2.0 Apparatus

2.1 Sampling

The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank.

2.1.1 Heated Probe

6.4 mm (1/4 in.) O.D. stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129°C (265°F).

The nozzle is an elbow fitting attached to the front end of the probe while the thermocouple is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil.

2.1.2 Filter Holder

25 mm (15/16 in.) I.D. Gelman filter holder with stainless steel body and stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

2.1.3 Filter Heating System

A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shelf capable of maintaining a gas temperature at the filter of 121 ± 3°C (250 ± 5°F).

2.1.4 Condensate Trap

9.5 mm (3/8 in.) I.D. 316 stainless steel tubing bent into a U-shape.

2.1.5 Valve

Stainless steel shut-off valve for starting and stopping sample flow.

2.1.6 Metering Valve

Stainless steel control valve for regulating the sample flow rate through the sample train.

2.1.7 Rotameter

Glass tube with stainless steel fittings, capable of measuring sample flow in the range of 60 to 100 cc/min.

2.1.8 SampleTank

Stainless steel or aluminum tank with a minimum volume of 4 L.

2.1.9 Mercury Manometer or Absolute Pressure Gauge

Capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

2.1.10 Vacuum Pump

Capable of evacuating to an absolute pressure of 10 mmHg.

2.2 Condensate Recovery Apparatus

The system for the recovery of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (ICV).

2.2.1 Hea Source

Sufficient to heat the condensate trap (including connecting tubing) to a temperature of 200°C.

2.2.2 Heat Tape

Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100°C.

2.2.3 Oxidation Catalyst

A suitable length of 9.5 mm (3/8 in.) O.D. Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (1/8 in.) diameter 19 percent chromia on alumina pellets.

2.2.4 Water Trap

Leak proof, capable of removing moisture from the gas stream.

2.2.5 Syringe Port

A 6.4 mm (1/4 in.) O.D. stainless steel tee fitting with a rubber septum placed in the side arm.

2.2.6 NDIR Detector

Capable of indicating CO_2 concentration in the range of zero to 5 percent.

2.2.7 Flow Control Valve

Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

2.2.8 Intermediate Collection Vessel

Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 L are recommended.

2.2.9 Mercury Manometer or Absolute Pressure Gauge

Capable of measuring pressure to within 1 mmHg in the range of 0 to 900 mm.

2.2.10 Syringe

10 mL gas-tight, glass syringe equipped with an appropriate needle.

2.3 NMO Analyzer

The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID.

2.3.1 Oxidation Catalyst

A suitable length of 9.5 mm (3/8 in.) O.D. Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2 mm (1/8 in.) alumina pellets.

2.3.2 Reduction Catalyst

A 7.6 cm (3 in.) length of 6.4 mm (1/4 in.) O.D. Inconel tubing fully packed with 100-mesh pure nickel powder.

2.3.3 Separation Column(s)

A 30 cm (1 ft.) length of 3.2 mm (1/8 in.) O.D. stainless steel tubing packed with 60/80 mesh Unibeads is followed by a 61 cm (2 ft.) length of 3.2 mm (1/8 in.) O.D. stainless steel tubing packed with 60/80-mesh Carbosieve G.

2.3.4 Sample Injection System

A 10-port GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.3.5 FID

An FID meeting the following specifications:

2.3.5.1 Linearity

A linear response (±5 percent) over the operating range as demonstrated by the procedures established in Section 5.2.3.

2.3.5.2 Range

A full scale range of 10 to 50,000 ppm CH_4.

2.3.6 Data Recording System

Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.4 Other Analysis Apparatus

2.4.1 Barometer

2.4.2 Thermometer

2.4.3 Vacuum Pump

2.4.4 Syringes

2.4.5 Liquid Sample Injection Unit

3.0 Reagents

3.1 Sampling

The following are required for sampling:

3.1.1 Crushed dry ice.

3.1.2 Coarse quartz wool.

3.1.3 Filters, glass fiber filters, without organic binder.

3.2 NMO Analysis

The following gases are needed:

3.2.1 Carrier Gases

3.2.2 Fuel Gas

3.2.3 Combustion Gas

3.3 Condensate Analysis

The following gases are needed:

3.3.1 CarrierGas

3.3.2 Auxiliary O_2

3.3.3 Hexane

3.3.4 Decane

3.4 Calibration

For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder.

3.4.1 Oxidation Catalyst Efficiency Check Calibration Gas

3.4.2 FID Linearity and NMO Calibration Gases

3.4.3 CO_2 Calibration Gases

3.4.4 NMO Analyzer System Check Calibration Gases

3.4.4.1 Propane Mixture

3.4.4.2 Hexane

3.4.4.3 Toluene

3.4.4.4 Methanol

4.0 Procedure

4.1 Sampling

4.1.1 Cleaning Sampling Equipment

Before its initial use and after each subsequent use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated.

4.1.2 Sample Tank Evacuation and Leak Check

Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes.

4.1.3 Sample Train Assembly

Just before assembly, measure the tank vacuum using a mercury U-tube manometer or absolute pressure gauge. Record this vacuum, the ambient temperature, and the barometric pressure at this time.

4.1.4 Pretest Leak Check

A pretest leak check is required.

4.1.5 Sample Train Operation

[See 40 CFR 60 for details]

4.2 Sample Recovery

[See 40 CFR 60 for details]

4.3 Condensate Recovery

[See 40 CFR 60 for details]

4.3.1 Daily Performance Checks

Each day before analyzing any samples, perform the following tests:

4.3.1.1 Leak Check

[See 40 CFR 60 for details]

4.3.1.2 System Background Test

[See 40 CFR 60 for details]

4.3.1.3 Oxidation Catalyst Efficiency Check

Conduct a catalyst efficiency test as specified in Section 5.1.2 of this method.

4.3.2 Recovery of the Condensate Trap Sample

[See 40 CFR 60 for details]

4.4 Analysis

4.4.1 Daily Operations and Calibration Checks

4.4.2 Operating Conditions

4.4.3 Analysis of Recovered Condensate Sample

4.4.4 Analysis of Sample Tank

4.5 Audit Samples

5.0 Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery Apparatus

5.1.1 Carrier Gas and Auxiliary O_2 Blank Check

5.1.2 Catalyst Efficiency Check

5.1.3 System Performance Check

5.1.3.1 50 µL Hexane.

5.1.3.2 10 µL Hexane.

5.1.3.3 50 µL Decane.

5.1.3.4 10 µL Decane.

5.2 Initial NMO Analyzer Performance Test

5.2.1 Oxidation Catalyst Efficiency Check

5.2.2 Reduction Catalyst Efficiency Check

5.2.2 Analyzer Linearity Check and NMO Calibration

5.2.3 System Peformance Check

5.3 NMO Analyzer Daily Calibration

5.3.1 CO_2 Response Factor

5.3.2 NMO Response Factors

5.4 Sample Tank and ICV Volume

6.0 Calculations

All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

6.1 Nomenclature

6.2 Allowable Pressure Change

6.3 Sample Volume

6.4 Noncondensible Organics

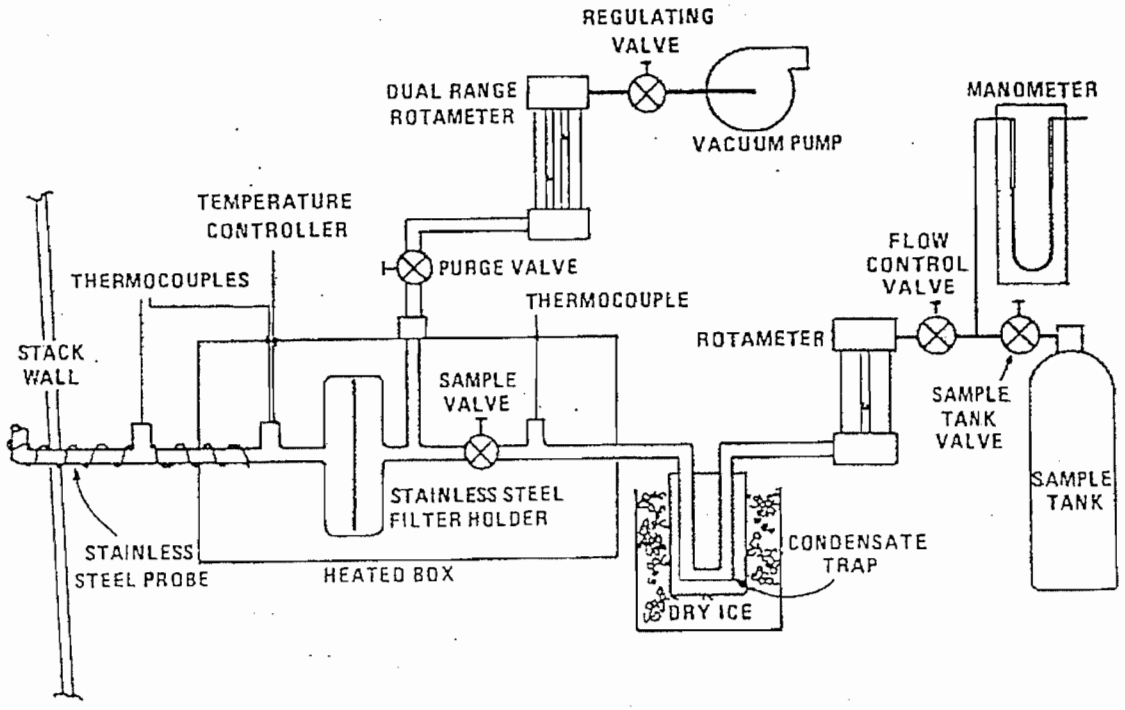
6.5 Condensible Organics

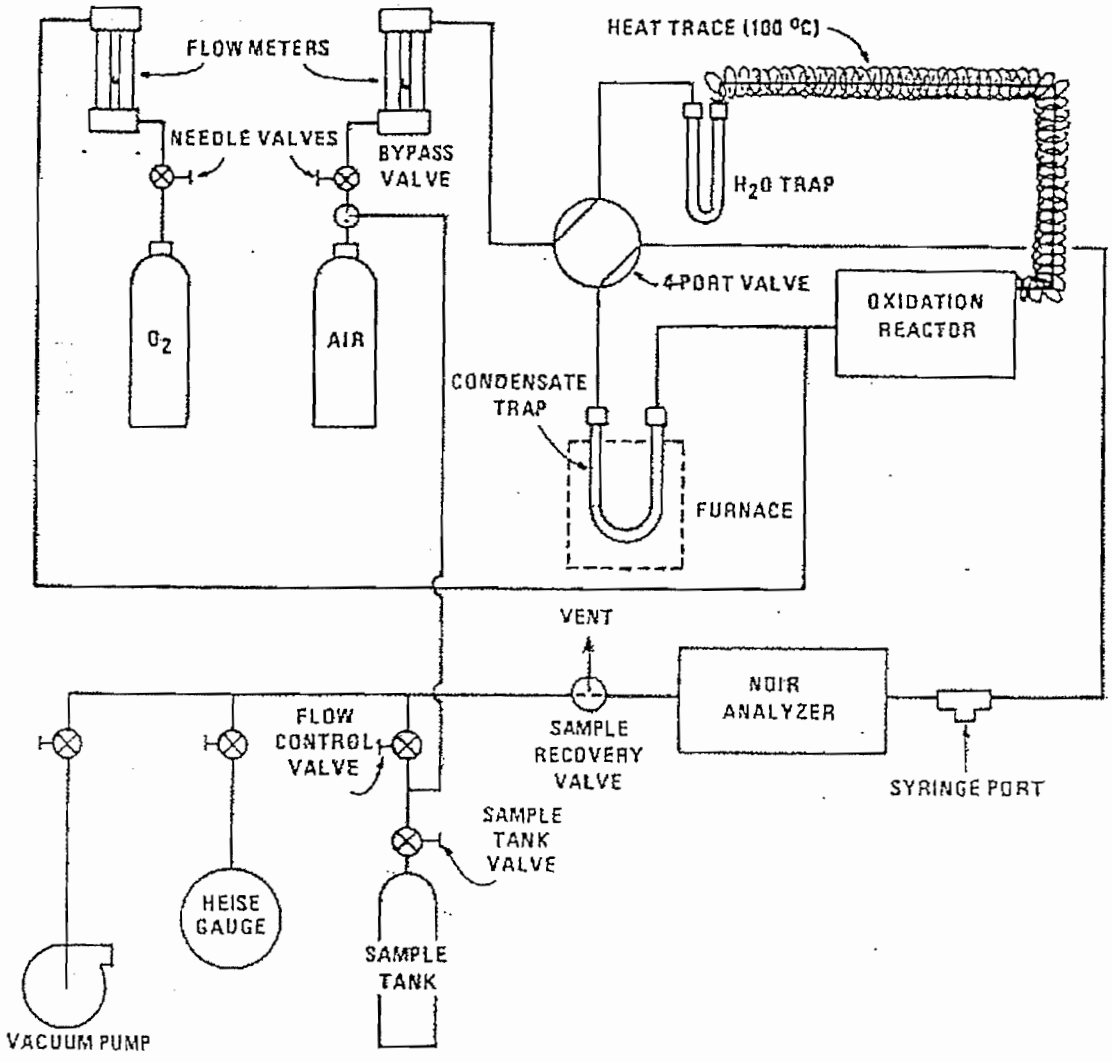
6.6 TGNMO

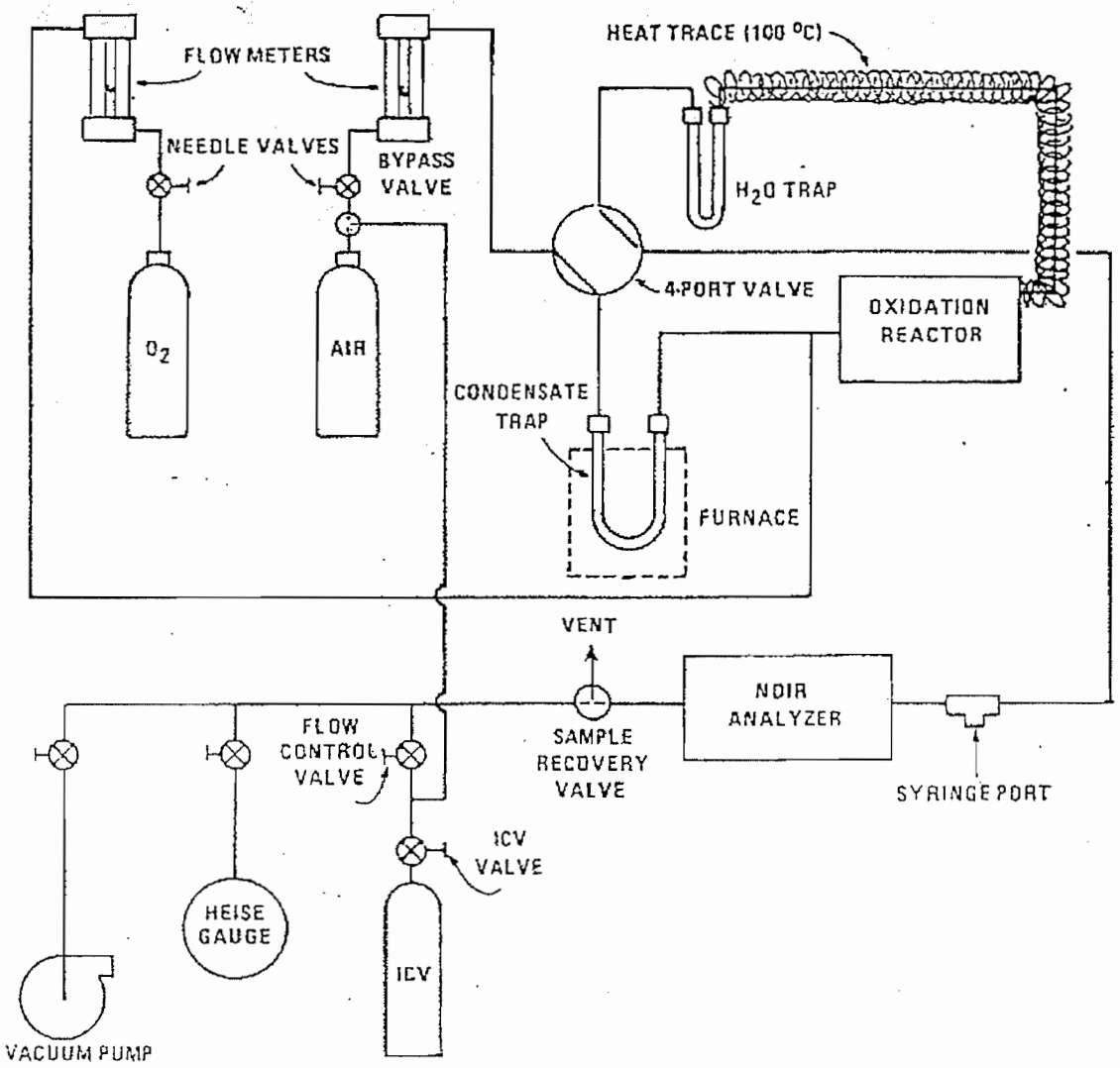
6.7 TGNMO Mass Concentration

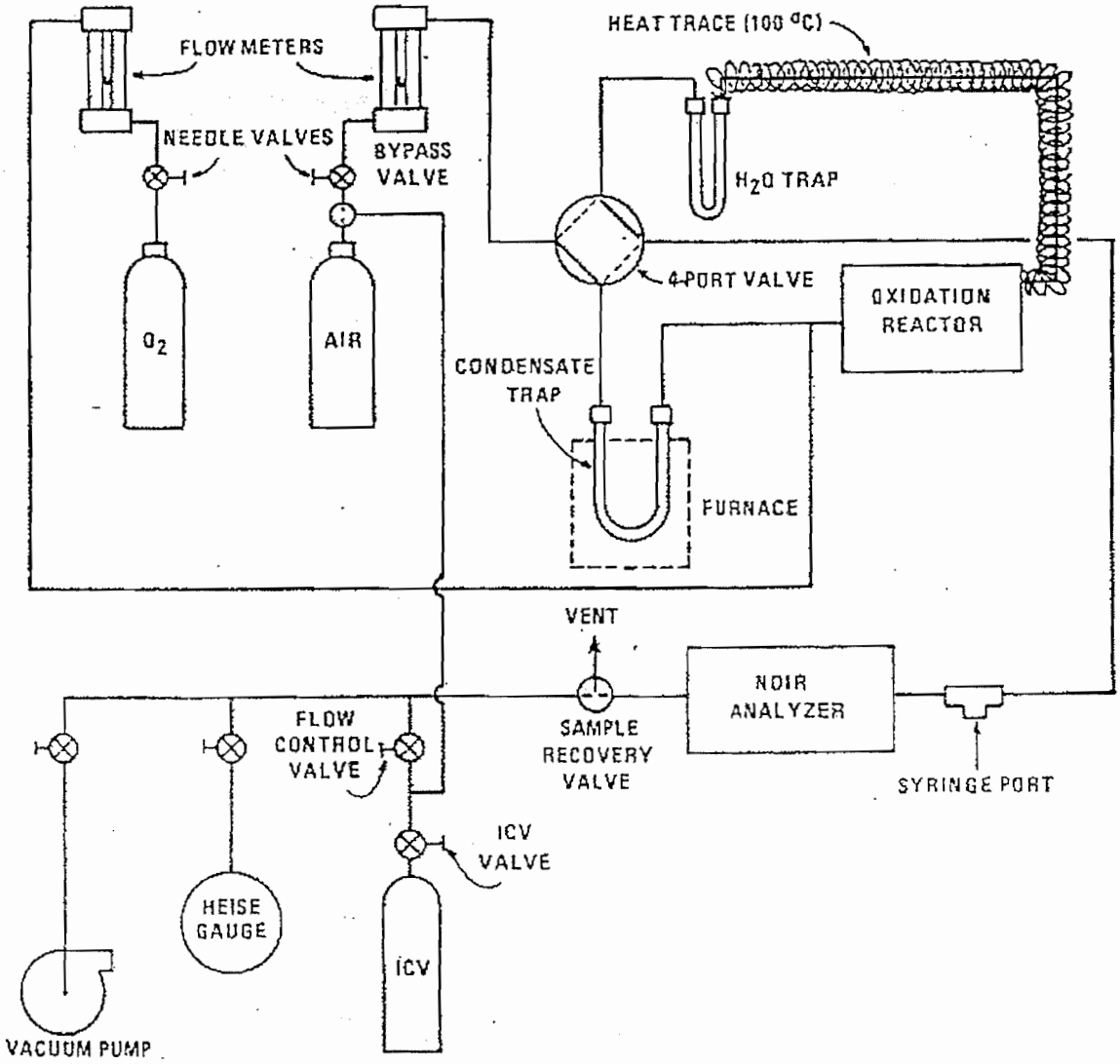
6.8 Percent Recovery

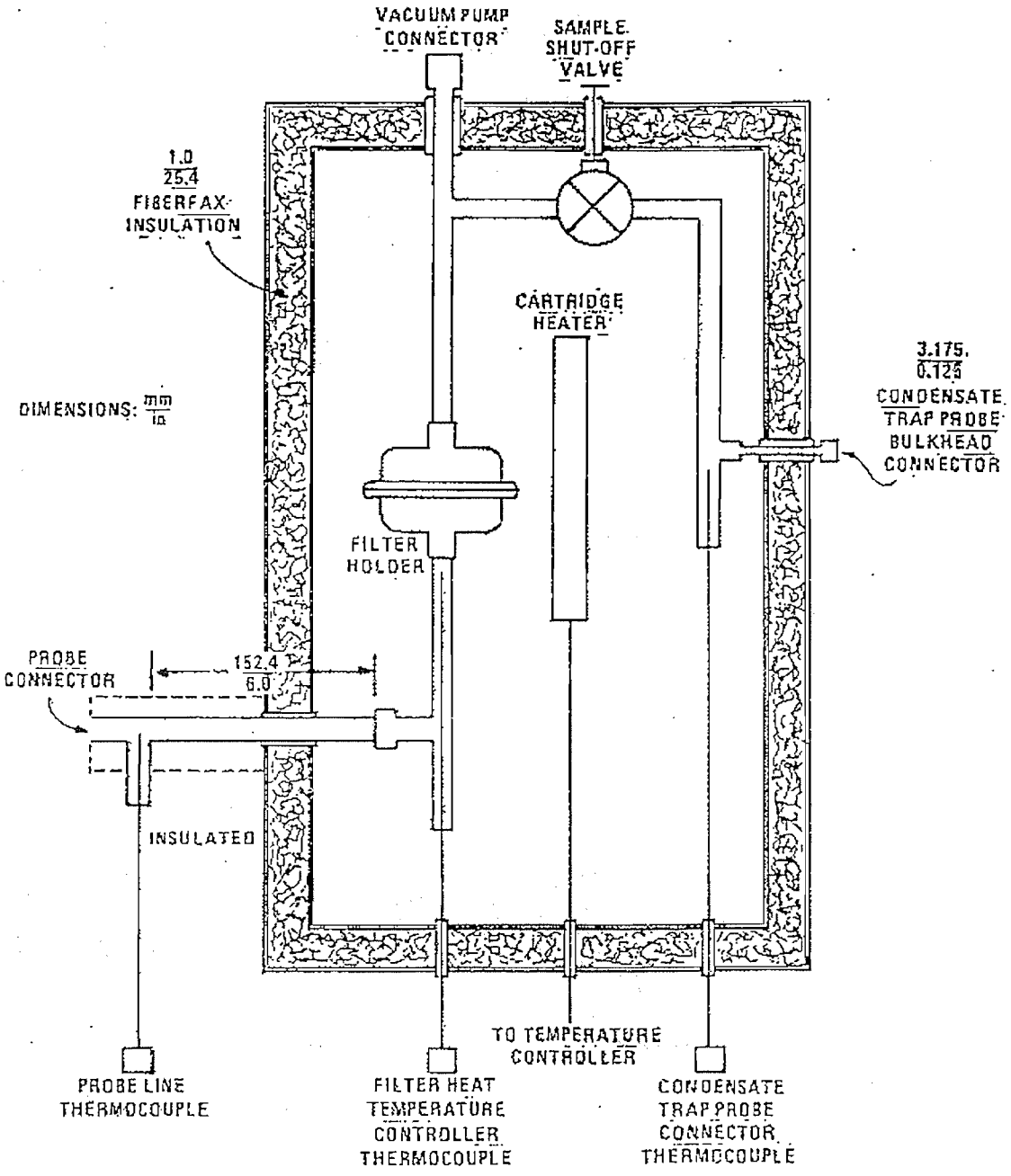
6.9 Relative Standard Deviation

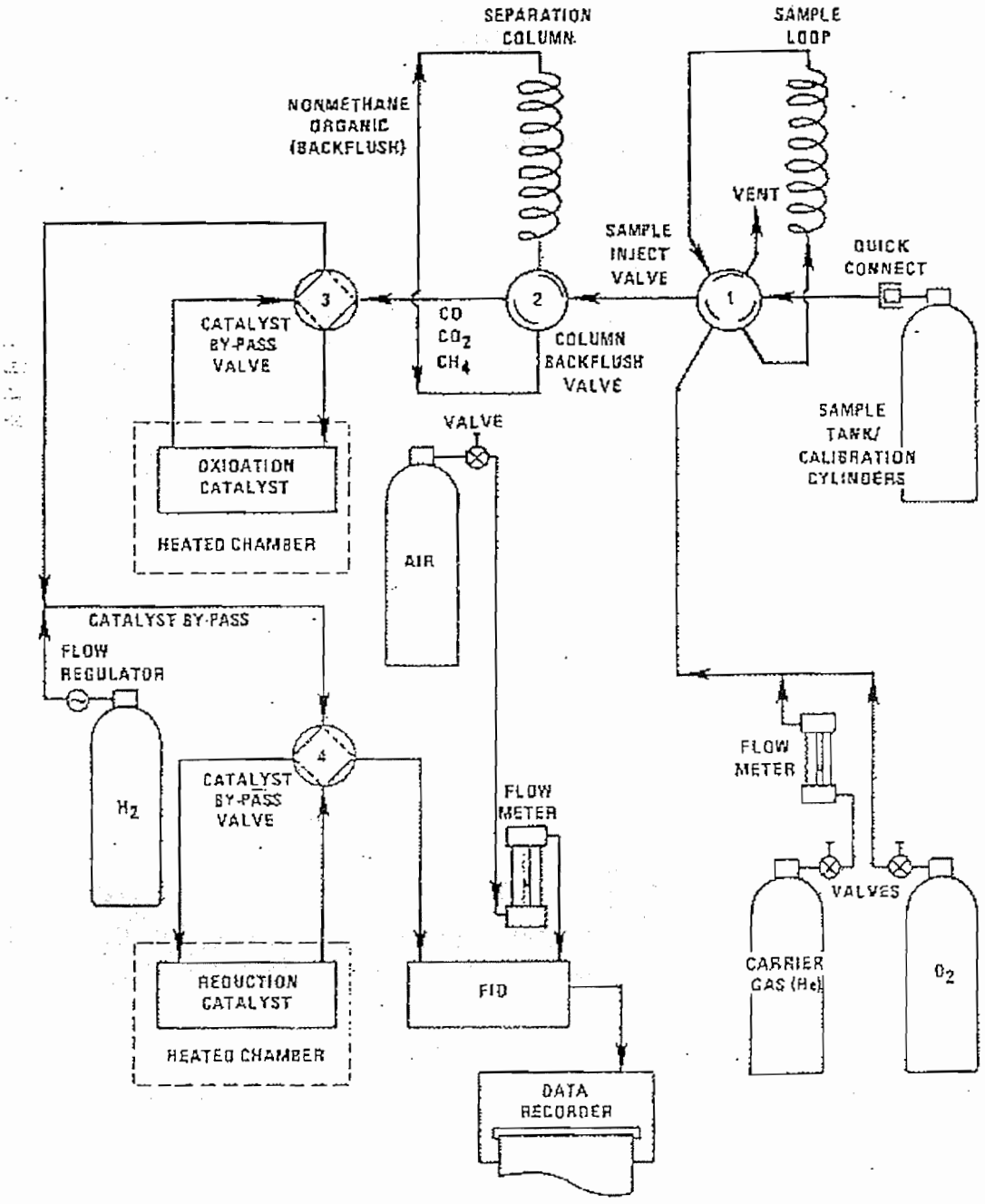

REGULATING VALVE
DUAL RANGE ROTAMETER
VACUUM PUMP
MANOMETER
TEMPERATURE CONTROLLER
THERMOCOUPLES
PURGE VALVE
THERMOCOUPLE
FLOW CONTROL VALVE
ROTAMETER
STACK WALL
SAMPLE VALVE
SAMPLE TANK VALVE
SAMPLE TANK
STAINLESS STEEL FILTER HOLDER
CONDENSATE TRAP
STAINLESS STEEL PROBE
HEATED BOX
DRY ICE


FLOW METERS
NEEDLE VALVES
BYPASS VALVE
HEAT TRACE (100 °C)
H_2O TRAP
4-PORT VALVE
OXIDATION REACTOR
O_2
AIR
CONDENSATE TRAP
FURNACE
VENT
NOIR ANALYZER
FLOW CONTROL VALVE
SAMPLE RECOVERY VALVE
SYRINGE PORT
SAMPLE TANK VALVE
HEISE GAUGE
SAMPLE TANK
VACUUM PUMP


FLOW METERS
NEEDLE VALVES
BYPASS VALVE
HEAT TRACE (100 °C)
H_2O TRAP
4-PORT VALVE
OXIDATION REACTOR
O_2
AIR
CONDENSATE TRAP
FURNACE
VENT
NDIR ANALYZER
FLOW CONTROL VALVE
SAMPLE RECOVERY VALVE
SYRINGE PORT
ICV VALVE
HEISE GAUGE
ICV
VACUUM PUMP


FLOW METERS
NEEDLE VALVES
BYPASS VALVE
HEAT TRACE (100 °C)
H2O TRAP
4-PORT VALVE
OXIDATION REACTOR
O2
AIR
CONDENSATE TRAP
FURNACE
VENT
NDIR ANALYZER
SAMPLE RECOVERY VALVE
SYRINGE PORT
FLOW CONTROL VALVE
ICV VALVE
HEISE GAUGE
ICV
VACUUM PUMP


VACUUM PUMP CONNECTOR
SAMPLE SHUT-OFF VALVE
1.0 25.4
FIBERFAX INSULATION
CARTRIDGE HEATER
3.175 0.125
CONDENSATE TRAP PROBE BULKHEAD CONNECTOR
DIMENSIONS: mm in
FILTER HOLDER
PROBE CONNECTOR
152.4 6.0
INSULATED
TO TEMPERATURE CONTROLLER
PROBE LINE THERMOCOUPLE
FILTER HEAT TEMPERATURE CONTROLLER THERMOCOUPLE
CONDENSATE TRAP PROBE CONNECTOR THERMOCOUPLE


SEPARATION COLUMN
SAMPLE LOOP
NONMETHANE ORGANIC (BACKFLUSH)
VENT
SAMPLE INJECT VALVE
QUICK CONNECT
CATALYST BY-PASS VALVE
CO
CO_2
CH_4
COLUMN BACKFLUSH VALVE
SAMPLE TANK/ CALIBRATION CYLINDERS
VALVE
OXIDATION CATALYST
HEATED CHAMBER
AIR
CATALYST BY-PASS
FLOW REGULATOR
FLOW METER
H_2
CATALYST BY-PASS VALVE
VALVES
REDUCTION CATALYST
FID
CARRIER GAS (He)
O_2
HEATED CHAMBER
DATA RECORDER

40 CFR 60, Method 25A (ABRIDGED)

Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

1.0 Principle and Applicability

1.1 Principle

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

1.2 Applicability

This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

2.0 Definitions

2.1 Measurement System

The system consists of the following major subsystems.

2.1.1 Sample Interface

That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 Organic Analyzer

That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 Span Value

The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 Calibration Gas

A known concentration of a gas in an appropriate diluent gas.

2.4 Zero Drift

The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift

The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.6 Response Time

The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error

The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3.0 Apparatus

The essential components of the measurement system are described below.

3.1 Organic Concentration Analyzer

An FIA capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe

Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is

collected from the centrally located 10 percent area of the stack cross section.

3.3 Sample Line

Stainless steel or Teflon tubing to transport the sample gas to the analyzer.

3.4 Calibration Valve Assembly

A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended.

3.5 Particulate Filter

An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant.

3.6 Recorder

A strip-chart recorder, analog computer, or digital recorder for recording measurement data.

NOTE: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4.0 Calibration and Other Gases

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders.

4.1 Fuel

A 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas

High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas

An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas

An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas

An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5.0 Measurement System Performance Specifications

5.1 Zero Drift

Less than ± 3 percent of the span value.

5.2 Calibration Drift

Less than ± 3 percent of span value.

5.3 Calibration Error

Less than ± 5 percent of the calibration gas value.

6.0 Pretest Preparations

6.1 Selection of Sampling Site

The location of the sampling site is generally specified by the applicable regulation or purpose of the test. The sample port shall be located at least 1.5 meters or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe

Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation

Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

6.4 Calibration Error Test

Immediately prior to the test series (within 2 hrs of the start of the test), introduce zero gas and high level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level

calibration gases and determine the differences between the measurement system responses and the predicted responses.

6.5 Response Time Test

Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7.0 Emission Measurement Test Procedure

7.1 Organic Measurement

Begin sampling at the start of the test period, recording time and any required process information as appropriate.

7.2 Drift Determination

Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.)

8.0 Organic Concentration Calculations

Determine the average organic concentration in terms of ppm, as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

9.0 Bibliography

40 CFR 60, Method 25B (ABRIDGED)

Determination of Total Gaseous Organic Concentration Using a Nondispersive Infrared Analyzer

This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Persons using this method should have a thorough knowledge of the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes

1.2 Applicability

This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes.

1.3 Data Quality Objectives

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

A gas sample is extracted from the source through a heated sample line, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

Same as Method 25A, Section 3.0.

4.0 Interferences

5.0 Safety

5.1 Disclaimer

This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Explosive Atmosphere

This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, Section 6.0, with some exception.

6.1 Organic Concentration Analyzer

A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, Section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, Section 8.0.

9.0 Quality Control

Same as Method 25A, Section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, Section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see Section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, Section 12.0.

13.0 Method Performance

14.0 Pollution Prevention

15.0 Waste Management

16.0 References

Same as Method 25A, Section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

40 CFR 60, Method 26 (ABRIDGED)

Determination of Hydrogen Halide and Halogen Emissions From Stationary Sources, Non-isokinetic Method

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 An integrated sample is extracted from the source and passed through a pre-purged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions, which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which are disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_x) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels.

4.4 A glass wool plug should <u>not</u> be used to remove particulate matter because a negative bias in the data could result.

4.5 There is anecdotal evidence that HF may be outgassed from new teflon components. If HF is a target analyte, then preconditioning of new teflon components, by heating should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before using this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. One mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 Sampling. The sampling train component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system to prevent moisture condensation. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream (see Section 6.1.6).

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation.

6.1.3 Impingers. Four 30 mL midget impingers with leak-free glass connectors.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6 to 16-mesh indicating type silica gel, or equivalent.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder greater than 120°C (248°F) during sampling.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 L/min (0.07 ft^3/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 L/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 L/min (0.2 ft^3/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500 mL or larger, two.

6.2.2 Storage Bottles. 100 or 250 mL, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100 mL size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade).

7.1 Sampling.

7.1.1 Filter. A 25-mm (1-in.)(or other size) Teflon glass mat. This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193-77 or 91, Type 3.

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4).

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH).

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110°C (230°F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing.

7.2.4 Chromatographic Eluent.

7.3 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 mL of the acidic absorbing solution into each one of the first pair of impingers, and 15 mL of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock.

8.1.3 Leak Check Procedure.

8.1.3.1 Sampling Train. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak checked separately.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe. Turn on the purge pump, and adjust the purge rate to 2 L/min (0.07 ft^3/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train. Adjust the sampling rate to 2 L/min and maintain this rate to within 10 percent during the entire sampling run.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle.

8.2.3 Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, pre-labeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled.

8.3 Sample Preparation for Analysis.

9.0 Quality Control

10.0 Calibration and Standardization

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6.

10.2 Ion Chromatograph.

10.2.1 Prepare the calibration standard.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values.

10.2.5 Draw a smooth curve using linear regression.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 IC conditions

11.1.2 Establish a stable baseline.

11.1.3 Inject in duplicate the reagent blanks, quality control sample, and the field samples.

11.2 Audit Sample Analysis.

11.2.1 A set of two EPA audit samples must be analyzed, subject to availability.

11.2.2 Concurrently analyze the audit samples and the compliance samples.

11.2.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples.

11.3 Audit Sample Results.

11.3.1 Calculate the concentrations in mg/L of audit sample.

11.3.2 Report the results of the audit samples and the compliance determination samples.

11.3.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations.

11.3.4 Failure to meet the 10 percent specification may require re-tests.

12.0 Data Analysis and Calculations

12.1 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions.

12.2 Sample Volume, Dry Basis, Corrected to Standard Conditions.

Calculate the sample volume.

12.3 Total μg HCl, HBr, or HF per Sample.

Concentrations of hydrogen halide or halogen in flue gas.

13.0 Method Performance

13.1 Precision and Bias.

13.2 Sample Stability.

13.3 Detection Limit

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

40 CFR 60, Method 26A (ABRIDGED)

Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources, Isokinetic Method

NOTE: This method does not include all of the specifications (e.g. equipment and supplies) and procedures (e.g. sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods. To obtain reliable results, a thorough knowledge of test methods 2, 5, and 26 is required.

1.0 Scope and Application

1.1 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources controlled by wet scrubbers, emitting acid particulate matter.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected on a filter and in absorbing solutions. An optional cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO).

NOTE: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), are potential interferents. Interferents for the halide measurements are the halogen gases.

4.2 The simultaneous presence of both HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_x) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes.

5.2.1 Sodium Hydroxide (NaOH).

5.2.2 Sulfuric Acid (H_2SO_4).

6.0 Equipment and Supplies

6.1 Sampling. The apparatus in the sampling train is similar to the Method 5 train.

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5.

6.1.2 Probe Liner. Same as Method 5.

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is saturated with moisture.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket.

6.1.6 Impinger Train. Five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should contain 50 mL of 0.1 N H_2SO_4. The following two impingers (acid impingers) contain 100 mL of 0.1 N H_2SO_4 each and shall be of the Greenburg-Smith design with the standard tip (Method 5). The next two impingers (alkaline impingers) each contain 100 mL of 0.1 N NaOH. The last impinger (containing silica gel) shall be of the modified Greenburg-Smith design (Method 5).

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder greater than 120°C (248°F) during sampling.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20-mesh sodium hydroxide-coated silica, or equivalent.

6.2 Sample Recovery.

6.2.1 Probe Liner and Probe Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel.

6.2.3 Funnels. Glass or high-density polyethylene.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment.

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade).

7.1 Sampling.

7.1.1 Filter. Teflon mat filter.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193-77 or 91, Type 3 (incorporated by reference - see 60.17).

7.1.3 Acidic Absorbing Solution. 0.1 N Sulfuric Acid (H_2SO_4).

7.1.4 Silica Gel. Crushed Ice, and Stopcock Grease. Same as Method 5.

7.1.5 Alkaline Absorbing Solution. 0.1 N Sodium Hydroxide (NaOH).

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3 5 H_2O$).

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride

(NaCl), sodium bromide (NaBr), and sodium fluoride (NaF).

7.2.4 Chromatographic Eluent. Same as Method 26, Section 7.2.4.

7.2.5 Water. Same as Section 7.1.2.

7.2.6 Acetone. Same as Method 5.

7.3 Quality Assurance Audit Samples.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Testers and analysts should be trained and experienced with the procedures to ensure reliable results.

8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, except for the following variations: Add 50 mL of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 mL of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 mL of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last impinger.

8.1.4 Leak Check Procedures. Follow the leak check procedures given in Method 5: Pretest Leak Check, Leak Checks During the Sample Run, and Post-Test Leak Check.

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) of greater than 120°C (248°F) because it is extremely difficult to purge acid gases off these components.

8.1.6 Post-Test Moisture Removal (Optional).

8.2 Sample Recovery.

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination).

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination).

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, Container No. 3.

8.2.6 Container Nos. 6 through 9 (Reagent Blanks).

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

9.2 Volume Metering System Checks. Same as Method 5.

10.0 Calibration and Standardization

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak Check of Metering System, and Barometer. Same as Method 5.

10.2 Ion Chromatograph.

10.2.1 Prepare the calibration standards.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in g/mL.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used.

11.1.2 Before sample analysis, establish a stable baseline.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples.

11.2 Container Nos. 1 and 2 and Acetone Blank. Same as Method 5.

11.3 Container No. 5. Same as Method 5, for silica gel.

11.4 Audit Sample Analysis.

11.4.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two EPA audit samples must be analyzed, subject to availability.

11.4.2 Concurrently analyze the audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

11.4.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples.

11.5 Audit Sample Results.

11.5.1 Calculate the concentrations in mg/L of audit sample and submit results.

11.5.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority.

11.5.3 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations.

11.5.4 Failure to meet the 10 percent specification may require retests until the audit problems are resolved.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature. Same as Method 5.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions.

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop.

12.4 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method, using the equations in Method 5.

12.6 Isokinetic Variation and Acceptable Results. Use Method 5.

12.7 Concentration. For particulate determination.

12.8 Total μg Cl_2 or Br_2 per Sample.

12.9 Concentration of Hydrogen Halide or Halogen in Flue Gas.

12.10 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, using data obtained in this method and the equations in Method 2.

13.0 Method Performance

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl due to reaction with small amounts of moisture in the probe and filter.

13.2 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks for analysis for HCl and Cl_2.

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2 g/mL.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

40 CFR 51, Method 202 (ABRIDGED)

Determination of Condensable Particulate Emissions From Stationary Sources

1.0 Principle and Applicability

1.1 Principle

1.1.1 Methodology

The condensable particulate matter (CPM) is collected in the impinger portion of a Method 17 (Appendix B, 40 CFR part 60) type sample train. The impinger contents are immediately purged after the run with nitrogen (N_2) to remove dissolved sulfur dioxide (SO_2) gases from the impinger contents. The impinger solution is then extracted with methylene chloride ($MeCl_2$) The organic and aqueous fractions are then taken to dryness and the residues weighed. The total of both fractions represents the CPM.

1.1.2 Collection Efficiency

The potential for low collection efficiency exist at oil-fired boilers. To improve the collection efficiency at these type of sources, an additional filter placed between the second and third impinger is recommended.

1.2 Applicability

1.2.1 CPM from Stationary Sources

This method applies to the determination of CPM emissions from stationary sources. It is intended to represent condensable matter as material that condenses after passing through a filter and as measured by this method.

This method may be used in conjunction with Method 201 or 201A if the probes are glass-lined.

1.2.2 Modification of Methodology

This method may also be modified to measure material that condenses at other temperatures by specifying the filter and probe temperature. A heated Method 5 out-of-stack filter may be used instead of the in-stack filter to determine condensable emissions at wet sources.

2.0 Precision and Interference

2.1 Precision

The precision, based on method development tests at an oil-fired boilers and a catalytic crackers, is 11.7 and 4.8 percent, respectively.

2.2 Interference

In sources that use ammonia injection as a control technique for hydrogen chloride (HCl), the ammonia interferes by reacting with HCl in the gas stream to form ammonium chloride (NH_4Cl) which would be measured as CPM. The sample may be analyzed for chloride and the equivalent amount of NH_4Cl can be subtracted from the CPM weight. However, if NH_4Cl is to be counted as CPM, the inorganic fraction should be taken to near dryness (less than 1 mL liquid) in the oven and then allowed to air dry at ambient temperature to prevent any NH_4Cl from vaporizing.

3.0 Apparatus

3.1 Sampling Train

Same as in Method 17, Section 2.1, with the exceptions noted below.

3.1.1 Probe Extension

The probe extension shall be glass-lined or Teflon.

3.1.2 Impingers

Both the first and second impingers shall be of the Greenburg-Smith design with the standard tip.

3.1.3 Cleaning of Glassware

All sampling train glassware shall be cleaned prior to the test with soap and tap water.

3.2 Sample Recovery

Same as in Method 17, Section 2.2, with the following additions.

3.2.1 N_2 Purge Line

Inert tubing and fittings capable of delivering 0 to 28 L/min of N_2 gas to the impinger train from a standard gas cylinder.

3.2.2 Rotameter

Capable of measuring gas flow at 20 L/min.

3.3 Analysis

The following equipment is necessary in addition to that listed in Method 17, Section 2.3.

3.3.1 Separatory funnel.

3.3.2 Weighing tins, 350-mL.

3.3.3 Dry equipment hot plate and oven with temperature control.

3.3.4 Pipets, 5 mL.

3.3.5 Ion Chromatograph, same as in Method 5F.

4.0 Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

4.1 Sampling

Same as in Method 17, Section 3.1 with the addition of deionized distilled water to conform to the American Society for Testing and Materials Specification D 1193-74, Type I I and the omission of Section 3.1.4.

4.2 Sample Recovery

Same as in Method 17, Section 3.2, with the following additions.

4.2.1 N_2 Gas

Zero N_2 gas at delivery pressures high enough to provide a flow of 20 L/min. for 1 hour through the sampling train.

4.2.2 Methylene Chloride, ACS grade

Blanks shall be run prior to use and only methylene chloride with low blank values (0.001 percent) shall be used.

4.2.3 Water

Same as in Section 4.1.

4.3 Analysis

Same as in Method 17, Section 3.3, with the following additions.

4.3.1 Methylene Chloride

4.3.2 Ammonium Hydroxide

4.3.3 Water

4.3.4 Phenolphthalein

5.0 Procedure

5.1 Sampling

Same as in Method 17, Section 4.1, with the following exceptions:

5.1.1 Charging Impingers

Place 100 mL of water in the first three impingers.

5.1.2 Use of Silicone Grease

Silicone grease in train assembly is not recommended.

5.2 Sample Recovery

Same as in Method 17, Section 4.2 with the addition of a post-test N_2 purge and specific changes in handling of individual samples.

5.2.1 Post-test N_2 Purge for Sources Emitting SO_2

NOTE: This step is recommended, but is optional.

5.2.2 Sample Handling

5.2.2.1 Sample Containers

Container Nos. 1, 2, and 3. If filter catch is to be determined, as detailed in Method 17, Section 4.2.

5.2.2.2 Container No. 4 (Impinger Contents)

Measure the liquid in the first three impingers to within 1 mL using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present.

5.2.2.3 Container No. 5 ($MeCl_2$ Rinse)

Follow the water rinses of each impinger and the connecting glassware, including the probe extension with two rinses of $MeCl_2$; save the rinse products in a clean, glass sample jar. Mark the liquid level on the jar.

5.2.2.4 Container No. 6 (Water Blank)

Once during each field test, place 500 mL of water in a separate sample container.

5.2.2.5 Container No. 7 ($MeCl_2$ Blank)

Once during each field test, place in a separate glass sample jar a volume of $MeCl_2$ approximately equivalent to the

volume used to conduct the $MeCl_2$ rinse of the impingers.

5.3 Analysis

Record the data required on a sheet.

5.3.1 Container Nos. 1, 2, and 3

5.3.2 Container Nos. 4 and 5

5.3.2.1 Extraction

5.3.2.2 Organic Fraction Weight Determination

5.3.2.3 Inorganic Fraction Weight Determination.

5.3.2.4 Analysis of Sulfate by IC

Determine the ammonium ion (NH_4^+) retained in the sample.

5.3.3 Analysis of Water and $MeCl_2$ Blanks (Container Nos. 6 and 7)

5.3.4 Analysis of Acetone Blank (Container No. 8)

6.0 Calibration

Same as in Method 17, Section 5, except for the following.

6.1 IC Calibration

Same as Method 5F, Section 5.

6.2 Audit Procedure

Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

6.3 Audit Samples

6.3.1 Audit Sample Availability

Audit samples will be supplied only to enforcement agencies for compliance tests.

6.4 Audit Results

Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample.

7.0 Calculations

Same as in Method 17, Section 6.

7.1 Nomenclature

7.2 Correction for NH_4^+ and H_2O

Calculate the correction factor to subtract the NH_4^+ retained in the sample based on the IC SO_4^{-2} and if desired, add the combined water removed by the acid-base reaction.

7.3 Mass of Inorganic CPM

7.4 Concentration of CPM

8.0 Alternative Procedures

8.1 Determination of NH_4^+ Retained in Sample by Titration

8.1.1 Alternative Procedure

An alternative procedure to determine the amount of NH_4^+ added to the inorganic fraction by titration may be used.

8.1.2 Calculate Concentration

Calculate the concentration of SO_4^{-2} in the sample.

8.1.3 Calculation

Calculate the CPM as described in Section 7.

8.2 Analysis of Chlorides by IC

8.3 Air Purge to Remove SO_2 from Impinger Contents

8.4 Chloroform-Ether Extraction

8.4.1 Chloroform Extraction

8.4.2 Additional Extraction

8.4.3 Weight Determination

8.5 Improving Collection Efficiency

If low impinger collection efficiency is suspected, the following procedure may be used.

8.5.1 Out-of-Stack Filter

Place an out-of-stack filter as described in Method 8 between the second and third impingers.

8.5.2 Analysis of Filter

Recover and analyze the filter according to Method 17, Section 4.2.

8.5.3 Calculation

Calculate the concentration of CPM.

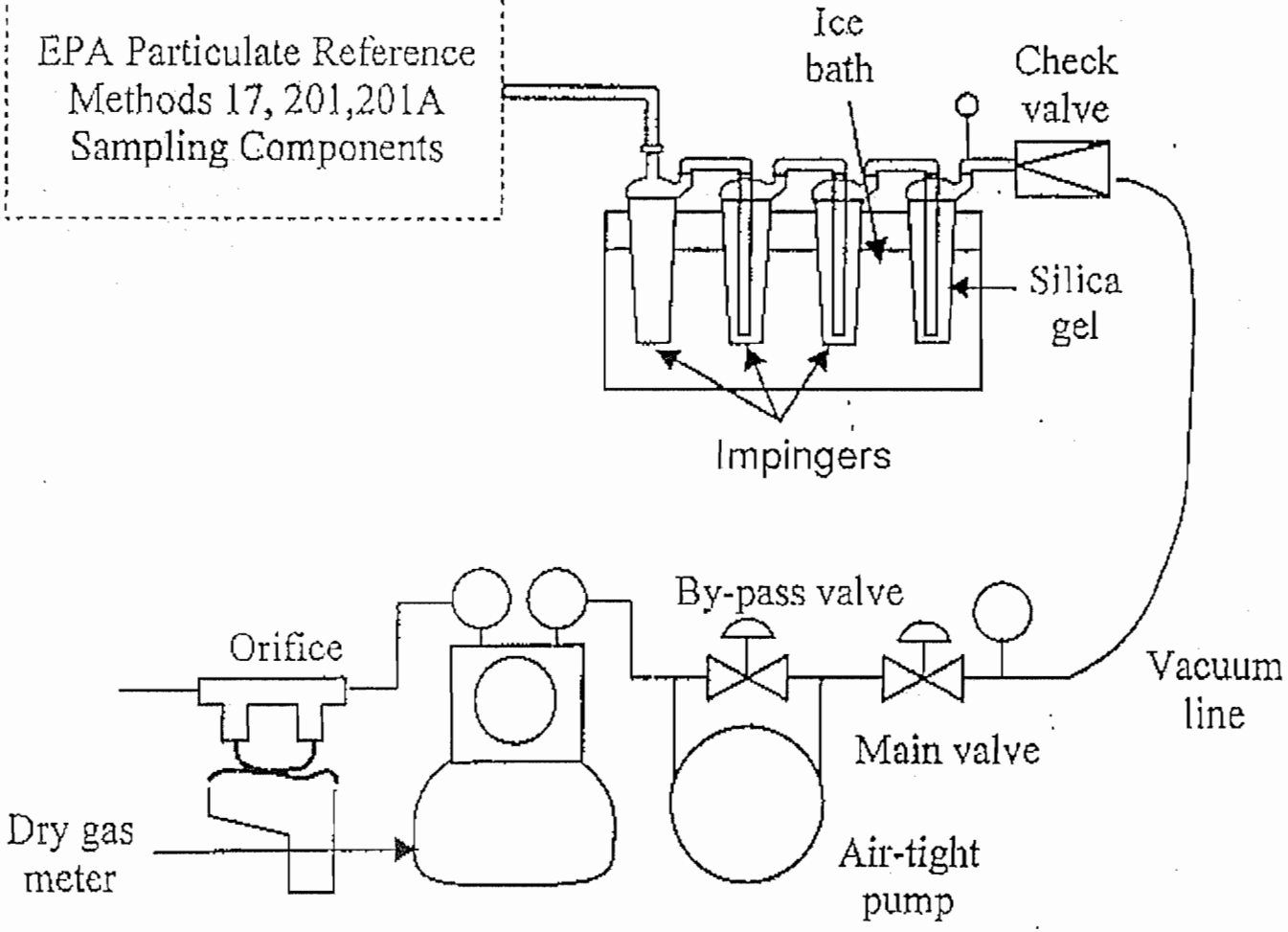
8.6 Wet Source Testing

When testing at a wet source, use a heated out-of-stack filter as described in Method 5.

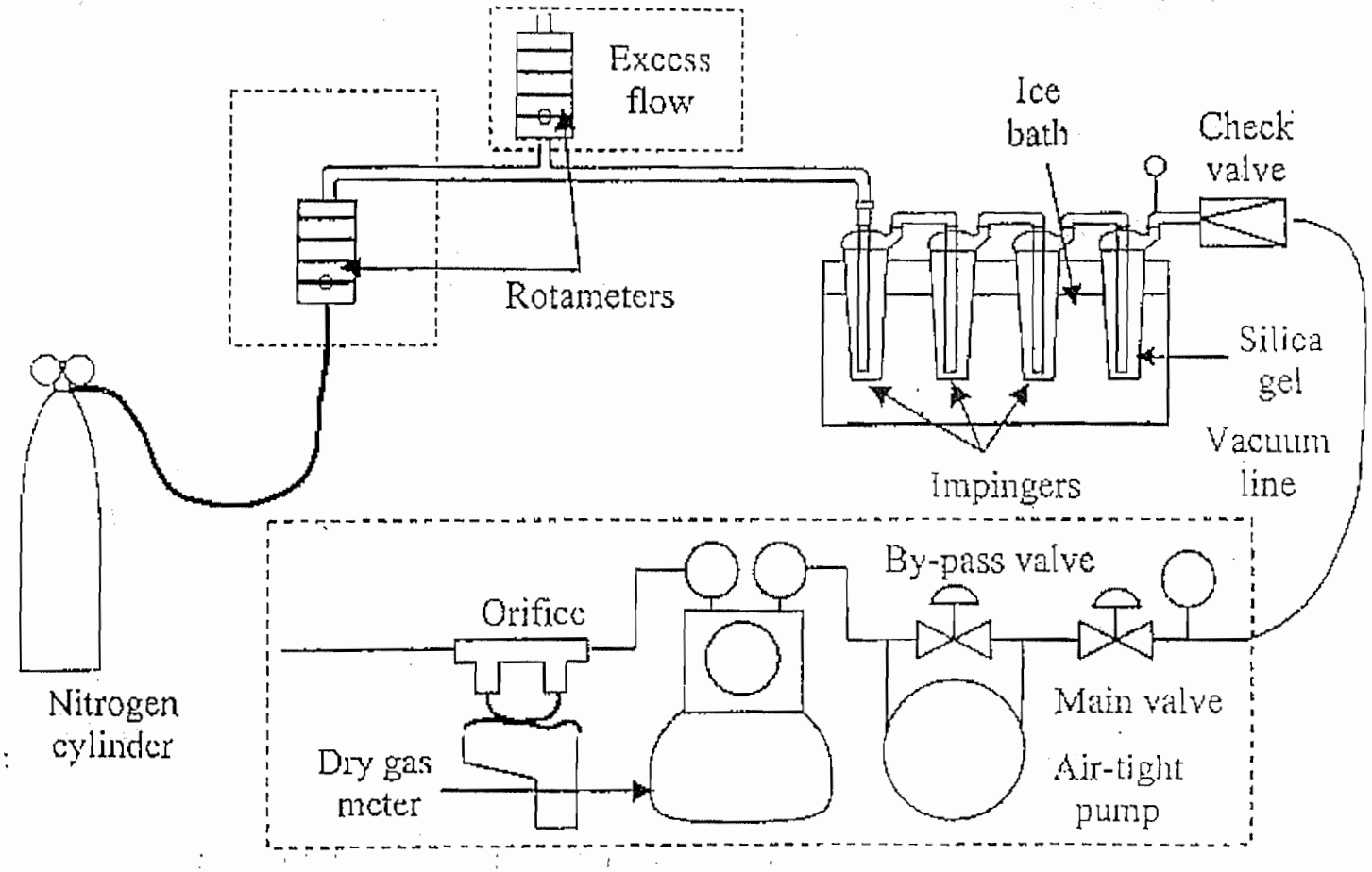
9.0 Bibliography

Method 202 Sampling Train

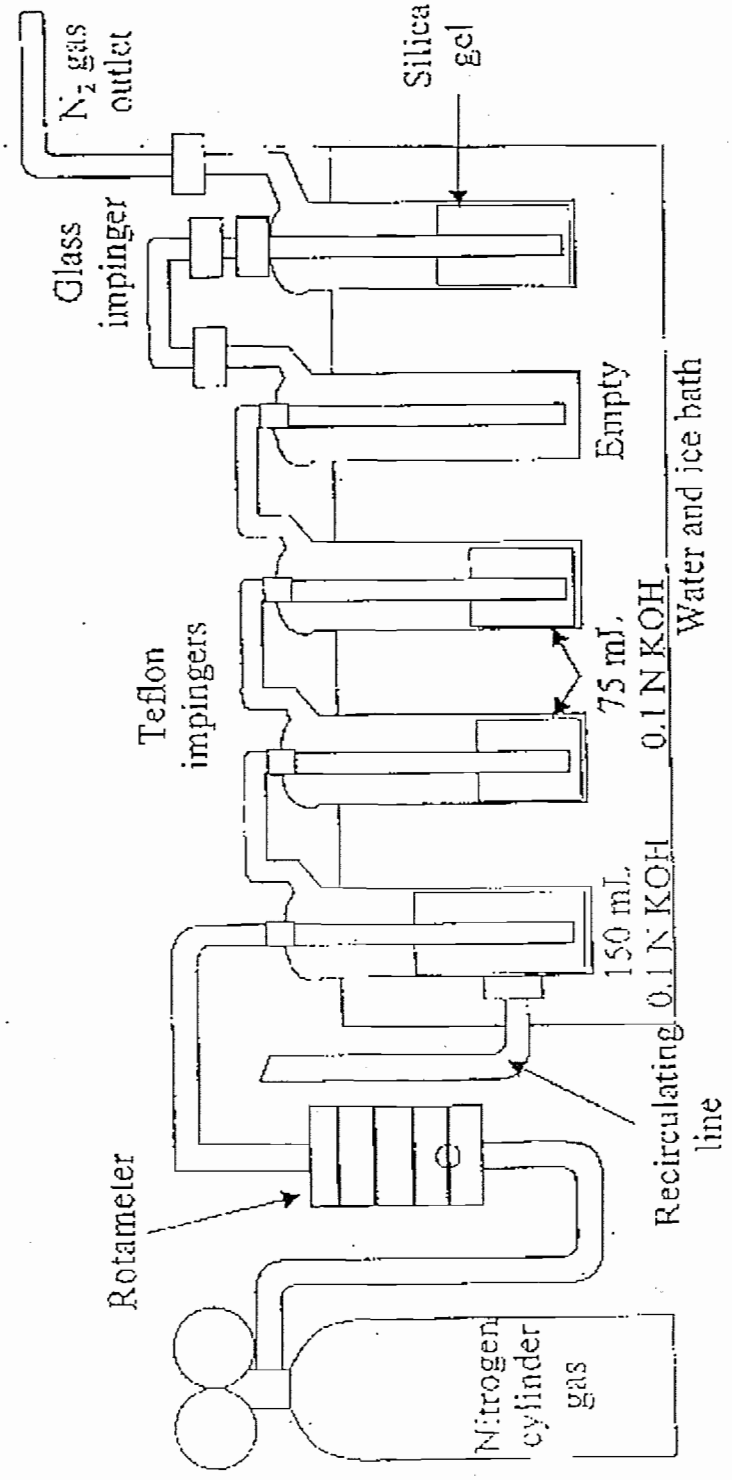
EPA Particulate Reference
Methods 17, 201,201A
Sampling Components



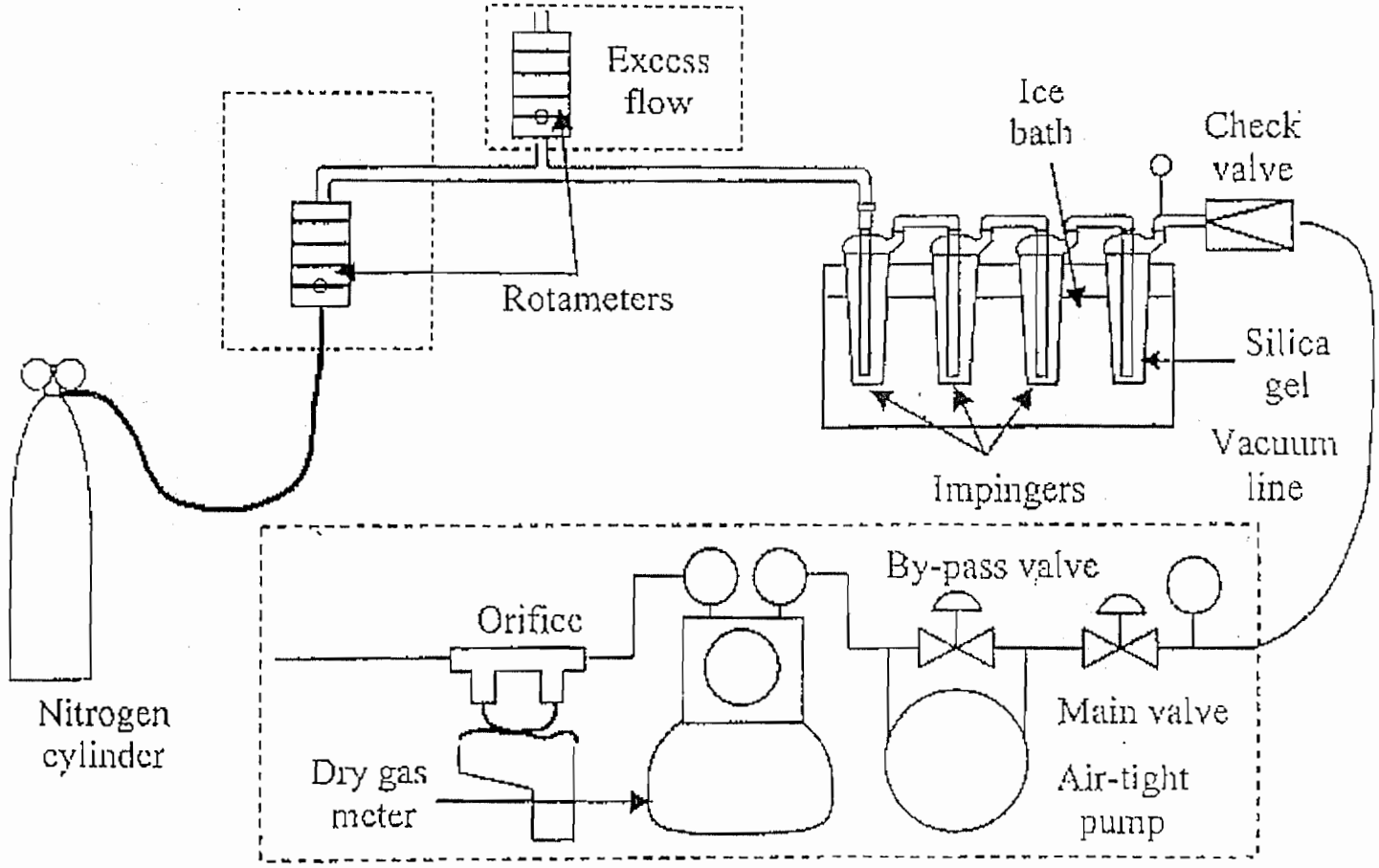
Method 202 Post Nitrogen Purge



Sample Train Post-Nitrogen Purge



Method 202 Post Nitrogen Purge



U.S. Environmental Protection Agency
Air Pollution Training Institute
Course #468
Compliance Test and Source Test Observation

Chapter

2

SW-846 Methods

The U. S. EPA's Office of Solid Waste (OSW), under the authority of the Resource Conservation and Recovery Act (RCRA), has developed a Compendium of test and analytical methods for use in determining regulatory compliance under RCRA. The title of the Compendium is *"Test Methods for Evaluating Solid Waste (SW-846)."* Except where mandated, SW-846 serves as a guidance document outlining criteria of acceptance in response to RCRA regulatory initiatives.

While the original intent of SW-846 was to address solid waste, it has been expanded to now include sampling and analytical methods associated with both ambient and source monitoring. This is due, in part, to the public outcry for EPA to monitor not only the water and soil pathways at hazardous waste sites utilizing incinerators as the method of destruction, but also to monitor the air pathway from the incinerator emissions in order to demonstrate compliance with national, state and local standards.

SW-S46 was conceived around 1980. Since that time, there have been several updates. The present regulatory status of the Compendium requires the use of the Third Edition methods (including Updates).

The basic question most frequently asked associated with SW-846 methods is: *"Are they EPA approved?"* Mr. Lesnik answered that question in his article entitled: *"Additional Perspective on SW-846. How and When Can Draft Methods Be Used?"* In that article, he states: *"U. S. EPA approval means that a method has been incorporated by reference in a Final Rule that has been published as* a *Federal Register Notice (FRN) either into SW-846 or directly into the RCRA regulations. In short, U. S. EPA-approved methods are promulgated methods that can be used without special permission for RCRA applications for which the use of SW-846 methods is mandatory". Therefore, until a method is promulgated by an* FRN, it *is not an approved method for these mandatory applications, no matter where it may be in the regulatory process."*

SW-846 methods are not published in the *Federal Register,* but are incorporated by reference in the appropriate RCRA regulations.

The present source test methods found in SW-846 were actually funded and developed by EPA's Office of Research and Development (ORD) through the Atmospheric Research and Exposure Assessment Laboratory (AREAL). Methods found in SW-846 have never been published in the *Federal Register* as reference methods.

SW-846, Method 0010 (ABRIDGED)

Modified Method 5 Sampling Train

1.0 Scope and Application

This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5.

2.0 Summary of Method

Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multi-component sampling train. Principal components of the train include a high efficiency glass or quartz fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semi-volatile organic species.

3.0 Interferences

Oxides of nitrogen (NO.) are possible interferants in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x, in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water soluble compounds from aqueous media.

4.0 Apparatus and Materials

4.1 SamplingTrain

4.1.1 Sampling Train Configuration

The sampling train configuration is adapted from EPA Method 5 procedures. The new components required are a condenser coil and a sorbent module, used to collect semi-volatile organic materials that pass through the glass or quartz fiber filter in the gas phase.

4.1.2 Construction Details

Construction details for the basic train components are given in APTD-0581.

4.1.3 Train Components

Basic operating and maintenance procedures for the sampling train are described in APTD-0576. The sampling train consists of the components detailed below.

4.1.3.1 Probe Nozzle

Stainless steel (316) or glass with sharp, tape red (300 angle) leading edge. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used.

4.1.3.2 Probe Liner

Borosilicate or quartz-glass tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 to 250°F) at the exit end during sampling.

4.1.3.3 Pitot Tube

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

4.1.3.4 Differential Pressure Gauge

Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2.

4.1.3.5 Filter Holder

Borosilicate glass, with a glass frit filter support and a sealing gasket.

4.1.3.6 Filter Heating System

Any heating system capable of maintaining a temperature of 120± 14°C (248 ±25°F) around the filter holder during sampling.

4.1.3.7 Organic Sampling Module

This unit consists of three sections, including a gas conditioning section, a

sorbent trap, and a condensate knockout trap.

4.1.3.8 Impinger Train

To determine the stack gas moisture content, four 500 mL impingers, connected in series with leak-free ground glass joints follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1/2 in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering System

The necessary components are a 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 1 percent, and related equipment.

4.1.3.10 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.

4.1.3.11 Gas Density Determination Equipment

Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3).

4.1.3.12 Calibration/Field Preparation Record

A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures.

4.2 Sample Recovery

4.2.1 Probe Liner

Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required.

4.2.2 Wash Bottles

Three Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used.

4.2.3 Glass Sample Storage Containers

Chemically resistant, borosilicate amber and clear glass bottles, 500 mL or 1,000 mL.

4.2.4 Petri Dishes

Glass, sealed around the circumference with wide (1 inch) Teflon tape.

4.2.5 Graduated Cylinder and/or Balances

To measure condensed water to the nearest 1 mL or 1 g.

4.2.6 Plastic Storage Containers

Screw cap polypropylene or polyethylene containers to store silica gel.

4.2.7 Funnel and Rubber Policeman

To aid in transfer of silica gel to container.

4.2.8 Funnels

Glass.

4.3 Filters

Glass or quartz-fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency.

4.4 Crushed Ice

Quantities ranging from 10-50 lbs. may be necessary.

4.5 Stopcock Grease

Solvent- insoluble, heat-stable silicone grease.

4.6 Glass Wool

To plug the unfritted end of the sorbent module.

5.0 Reagents

5.1 Adsorbent Resin

Porous polymeric resin (XAD-2 or equivalent) is recommended.

5.2 Silica Gel

Indicating type, 6-16 mesh.

5.3 Impinger Solutions

Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species.

5.4 Sample Recovery Reagents

5.4.1 Methylene Chloride

Distilled-in-glass grade is required for sample recovery and cleanup.

5.4.2 Methyl Alcohol

Distilled-in-glass grade is required for sample recovery and cleanup.

5.4.3 Water

Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 Sample Collection, Preservation, and Handling

6.1 Training

Because of complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory Preparation

6.2.1 Maintenance

6.2.2 Weighing

6.2.3 Filter Check

6.2.4 Desiccate Filters

6.3 Preliminary Field Determinations

6.3.1 Selection of Sampling Site

Select the sampling site and the minimum number of sampling points according to EPA Method 1. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6.

6.3.2 Nozzle Selection

Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates (see Section 2.2 of EPA Method 2).

6.3.3 Probe Liner Selection

Select a suitable probe liner and probe length so that all traverse points can be sampled.

6.3.4 Sample Volume

A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems.

6.3.5 Sample Time

Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement.

6.4 Preparation of Collection Train

6.4.1 Openings Closed

During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

6.4.2 Preparation of Sorbent Trap

Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin.

6.4.3 Preparation of Impinger Train

If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of pre-weighed silica gel from its container to the fourth impinger.

6.4.4 Placement of Filter

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 to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 Nozzle Installation

When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are < 260°C (500°F) and a woven glass-fiber gasket when temperatures are higher.

6.4.6 Set-up Sampling Train

Set up the sampling train. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

Place crushed ice around the impingers and the organic module condensate knockout.

6.4.7 Operation

Turn on the sorbent module and condenser coil coolant re-circulating pump and begin monitoring the sorbent module gas entry temperature.

Turn on and set the filter and probe heating systems at the desired operating temperatures.

6.5 Leak Check Procedures

6.5.1 Pre-Test Leak Check

6.5.1.1 A pre-test leak check is required.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures.

6.5.1.2 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 attaching a carbon-filled leak check impinger to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381mm Hg (15 inch 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.

6.5.1.3 The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached.

6.5.1.4 When the leak check is complete, slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable). When the vacuum drops to 127 mm (5 inch) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed.

6.5.2 Leak Checks During Sampling Run

6.5.2.1 Changing Components

If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary. a leak check shall be conducted immediately after the interruption of sampling and before the change is made.

6.5.2.2 Final Leak Check

Immediately after a component change, and before sampling is reinitiated, a leak check similar to a pretest leak check must be conducted.

6.5.3 Post-Test Leak Check

6.5.3.1 Mandatory Leak-check

A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done with the same procedures as those with the pre-test leak check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run.

6.6 Sampling Train Operation

6.6.1 Maintaining Isokinetic

During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic. Maintain a temperature around the filter of 120±14°C (248±25°F) and a gas temperature entering the sorbent trap at a maximum of 2°C (68°F).

6.6.2 Recording Data

For each run, record the data required on a field test data sheet. 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 inflow rates are made before and after each leak check, and when sampling is halted.

6.6.3 Sampling

Clean the stack access ports. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point. Immediately start the pump and adjust the flow to isokinetic conditions.

6.6.4 Negative Pressure

When the stack is under significant negative pressure, take care to close the coarse-adjust valve before inserting the probe into the stack.

6.6.5 Probe Position

When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

6.6.6 Traverse Stack Gas

Traverse the stack cross section as required by EPA Method 1.

6.6.7 Periodic Adjustments

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

6.6.8 Pressure Drop and Filter

If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. After a new filter/sorbent trap assembly is installed, conduct a leak check.

6.6.9 Single Sampling Train

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.

6.6.10 Separate Analysis

Note that when two or more trains are used, separate analysis of the front half organic module and impinger catches from each train shall be performed.

6.6.11 End of Sample Run

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. Also, leak check the pitot lines as described in EPA Method 2. The lines must pass this leak check in order to validate the velocity- head data.

6.6.12 Calculate Percent Isokinetics

Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 Sample Recovery

7.1 Preparation

7.1.1 Probe 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 the tip to prevent losing or gaining particulate matter.

7.1.2 Capping Probe

Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet. Remove the umbilical cord from the last impinger and cap the impinger.

7.1.3 Cap the Filter

Cap the filter holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas conditioning section. Cap all organic module openings. Disconnect the organic module knockout trap from the impinger train inlet and cap both of these openings.

7.1.4 Transfer the Components

Transfer the probe, the filter, the organic module components, and the impinger/condenser assembly to the cleanup area.

7.1.5 Reagents Blanks

Save a portion of all washing solutions (methanol/ methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, pre-labeled glass sample container.

7.1.6 Abnormal Conditions

Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample Containers

7.2.1 Container No. 1

Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Label the container and seal with 1 in. wide Teflon tape around the circumference of the lid.

7.2.2 Container No. 2

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Perform rinses as follows:

7.2.2.1 Probe Nozzle Recovery

Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush.

7.2.2.2 Probe Recovery

Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Probe Recovery Rinse

Follow the solvent rinse with a probe brush. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 Team Work

It is recommended that two people work together to clean the probe to minimize sample losses.

7.2.2.5 Filter Holder Recovery

Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1: 1 v/v) mixture. Label the container to identify its contents.

7.2.3 Container No. 3

The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment.

7.2.4 Container No.4

Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL by using a graduated cylinder or by weighing to within ± 0.5 g using a triple-beam balance. Transfer this liquid to a pre-labeled glass sample container.

7.2.5 Container No. 5

All sampling train components located between the high-efficiency glass or quartz-fiber filter and the first wet impinger or the final condenser system (including the heated Teflon line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/m ethylene chloride (1:1 v/v) and the rinsings combined.

7.2.6 Container No. 6

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.

7.3 Impinger Water

7.3.1 Measure Liquid

Make a notation of any color or film in the liquid catch. Measure the liquid 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.

7.3.2 Discard Impinger Volume

Discard the liquid after measuring and recording the volume or weight.

7.3.3 Measure Condenser Water

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

7.4 Sample Preparation for Shipment

Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 Analysis

8.1 Sample Preparation

8.1.1 General

8.1.2 Condensate

8.1.3 Impinger

8.1.4 XAD-2

8.1.5 Particulate Filter (and Cyclone Catch)

8.1.6 Train Solvent Rinses

8.2 Sample Analysis

8.2.1 General

8.2.2 Operation of Mass Spectrometer

8.2.3 Electron Ionization Spectra

8.2.4 Chemical Ionization Spectra

9.0 Calibration

9.1 Probe Nozzle

Probe nozzles shall be calibrated before their initial use in the field.

9.2 Pitot Tube

The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84.

9.3 Metering System

9.3.1 Calibration of Metering System

Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576.

9.3.2 Intermediate Calibration

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). The vacuum shall be set at the maximum value reached during the test series.

9.3.3 Leak Check of Metering System

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.

9.4 Probe Heater

The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576.

9.5 Temperature Gauges

Each thermocouple must be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers must conform to ASTM E-1 63°C or 63°F specifications.

9.5.1 Three Point Calibration

Impinger, organic module, and dry gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, three-point calibration at ice water, room air, and boiling water temperatures is necessary.

9.5.2 Probe and Stack Thermocouple

For the thermocouples used to indicate the probe and stack temperatures, a three-point

calibration at ice water, boiling water, and hot oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5 percent at each of the calibration points.

9.6 Barometer

Adjust the barometer initially and before each test series to agree to within ± 25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-Beam Balance

Calibrate the triple-beam balance before each test series, using Class-S standard weights.

10.0 Calculations

10.1 Carry Out Calculations

Round off figures after the final calculation to the correct number of significant figures.

10.2 Nomenclature

10.3 Average Dry-Gas Meter Temperature and Average Orifice Pressure Drop

See field test data sheet.

10.4 Dry-Gas Volume

Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]).

If L(p) or L(i) exceeds L(a), modifcations to the equations must made.

a. Case I (no component changes made during sampling run): Replace with the expression

$$Vm - [LP - L_a]$$

b. Case II (one or more component changes made during the sampling run): Replace V with the expression:

$$L_p - L_a$$

10.5 Volume of Water Vapor

10.6 Moisture Content

10.7 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	$2X^{10-3}$
g/ft^3	g/m^3	35.31

10.8 Isokinetic Variation

10.8.1 Calculation from Raw Data

10.8.2 Calculation for Intermediate Values

10.8.3 Acceptable Results

If 90 percent < I<-110 percent, the results are acceptable.

10.9 Determination of Minimum Sample Volume

To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 General

From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent:

10.9.2 Average Discharge Concentration

The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source.

10.9.3 Safety Margin

In making this calculation, it is recommended that a safety margin of at least ten be included:

10.10 Concentration of Any Given POHC in the Gaseous Emissions of a Combustion Process:

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

2) Sum the amount of POHC found in all samples associated with a single train.

3) Divide the total ug found by the volume of stack gas sampled (m^3).

11.0 Quality Control

11.1 Sampling

See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis

11.2.1 Field Blanks

11.2.2 Method Blanks

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 Method Performance

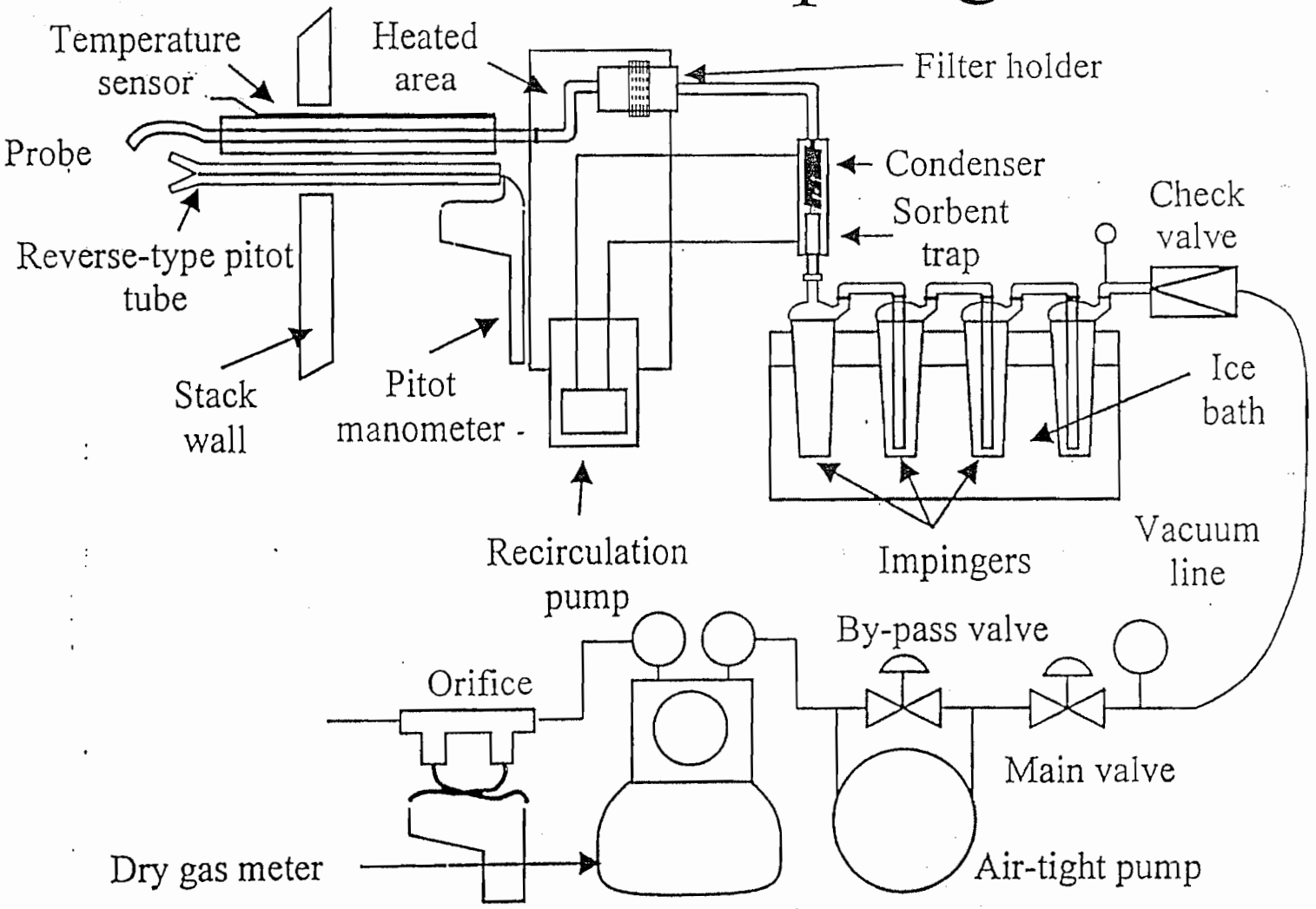
12.1 Method Performance Evaluation

12.2 Method Detection Limit

12.3 Method Precision and Bias

13.0 References

Method 0010 Sampling Train



SEMIVOST RECOVERY PROCEDURE

SW-846, Method 0030 (ABRIDGED)

Volatile Organic Sampling Train (VOST)

1.0 Introduction

This method describes the collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. For the purpose of definition, volatile POHCs are those POHCs with boiling points less than 100°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may break through the sorbent under the conditions of the sample collection procedure.

1.1 Scope and Application

Field application for POHCs of this type should be supported by laboratory data which demonstrate the efficiency of a volatile organic sampling train (VOST) to collect POHCs with boiling points less than 30°C. This may require using reduced sample volumes collected at flow rates between 250 and 500 mL/min. Many compounds which boil above 100°C (e.g., chlorobenzene) may also be efficiently collected and analyzed using this method.

1.1.1 This method employs a 20 L sample of effluent gas containing volatile POHCs which is withdrawn from a gaseous effluent source at a flow rate of 1 L/minute, using a glass-lined probe and a VOST. (Operation of the VOST under these conditions has been called FAST VOST.) The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax® and the second trap (back trap) contains approximately 1g each of Tenax® and petroleum based charcoal (SKC Lot 104 or equivalent), 3:1 by volume. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.2 An alternative set of conditions for sample collection has been used. This method involves collecting sample volume of 20 liters or less at reduced flow rate. (Operation of the VOST under these conditions has been referred to as SLO-VOST.) This method has been used to collect 5 liters of sample (0.25 L/minute for 20 minutes) or 20 liters of sample (0.5 L/minute for 40 minute) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 35°C. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.3 Analysis of the traps is carried out by thermal desorption purge and trap-by-gas chromatography/mass spectrometry (see Method 5040). The VOST is designed to be operated at 1 L/min with traps being replaced every 20 minutes for a total sampling time of 2 hours.

1.1.4 This method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators. This method is designed for use in calculating DRE for the volatile POHCs and to enable a determination that DRE values for removal of the volatile POHCs are equal to or greater than 99.99 percent.

1.1.5 The sensitivity of this method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is 0.1 pg/m^3 of flue gas, to permit calculation of a DRE equal to or greater than 99.99 percent for volatile POHCs which may be present in the waste stream at 100 ppm.

1.1.6 This method is recommended for use only by experienced sampling personnel and analytical chemists or under close supervision by such qualified persons.

1.1.7 Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many potential interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites.

1.1.8 To avoid or minimize the low-level contamination of train components with volatile POHCs, care should be taken to avoid contact of all interior surface or train components with synthetic organic materials and train components should be carefully cleaned and conditioned according to the procedures described in this protocol.

2.0 Apparatus

2.1 Volatile Organic Sampling Train

The VOST consists of a glass-lined probe followed by an isolation valve, a water-cooled glass condenser, a sorbent cartridge containing Tenax® (1.6 g), an empty impinger for condensate removal, a second water-cooled glass condenser, a second sorbent cartridge containing Tenax® and petroleum-based charcoal (3:1 by volume; approximately 1 g of each), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The gas pressure during sampling and for leak checking is monitored by pressure gauges which are in-line and downstream of the silica gel drying tube. The components of the sampling train are described below.

2.1.1 Probe

The probe should be made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is to be maintained above 130°C but low enough to ensure a resin temperature of 20°C. A water-cooled probe may be required at elevated stack temperatures to protect the probe and meet the above requirements. Isokinetic sample collection is not a requirement for the use of VOST since the compounds of interest are in the vapor phase at the point of sample collection.

2.1.2 Isolation Valve

The isolation valve should be a greaseless stopcock with a glass bore and sliding Teflon plug with Teflon wipers (Ace 8193 or equivalent).

2.1.3 Condensers

The condensers (Ace 5979-14 or equivalent) should be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent cartridge. The top connection of the condenser should be able to form a leak-free, vacuum-tight seal without using sealing greases.

2.1.4 SorbentCartridges

2.1.4.1 The sorbent cartridges used for the VOST may be used in either of two configurations: the inside/outside (1/0) configuration in which the cartridge is held within an outer glass tube and in a metal carrier, and the inside-inside (1/1) configuration in which only a single glass tube is used, with or without a metal carrier. In eithercase, the sorbent packing will be the same.

2.1.4.1.1 The first of a pair of sorbent cartridges shall be packed with approximately 1.6 g Tenax® QC resin and the second cartridge of a pair shall be packed with Tenax® QC and petroleum-based charcoal (3:1 by volume; approximately 1 g of each).

2.1.4.1.2 The second sorbent cartridge shall be packed so that the sample gas stream passes through the Tenax® layer first and then through the charcoal layer .

2.1.4.2 The sorbent cartridges shall be glass tubes with approximate dimensions of 10 cm by 1.6 cm I.D. The two acceptable designs (1/0, 1/1) for the sorbent cartridge are described in further detail below.

2.1.4.2.1 Inside Sorbent Cartridge

This cartridge is a single glass tube (10 cm by 1.6 cm I.D.) which has the ends reduced in size to accommodate a 1/4 or 3/8 in. Swagelok or Cajon gas fitting.

2.1.4.2.2 Inside Outside Type Sorbent Cartridge

In this design the sorbent materials are held in the glass tube with a fine mesh stainless steel screen and a C-clip. The glass tube is then placed within a large diameter glass tube and held in place using Vito 0-rings. The purpose of the outer glass tube is to protect the exterior of the resin-containing tube from contamination. The two glass tubes are held in a stainless steel cartridge holder, where the ends of the glass tubes are held in place by Viton 0-rings placed in machine grooves in each metal end piece.

2.1.5 Metering System

The metering system for VOST shall consist of vacuum gauges, a leak-free pump, a calibrated rotameter for monitoring the gas flow rate, a dry gas meter with 2 percent accuracy at the required sampling rate, and related valves and equipment.

2.1.6 Sample transfer lines

All sample transfer lines to connect the probe to the VOST shall be less than 5 feet in length, and shall be heat-traced Teflon with connecting fittings which are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

3.0 Reagents and Materials

3.1 2,6-Diphenylene Oxide Polymer (Tenax®, 35/60 Mesh)

3.1.1 The new Tenax® is **Soxhlet** extracted for 24 hours with methanol. The Tenax® is dried for 6 hours in a vacuum oven at 50°C before use.

3.1.2 If very high concentrations of volatile POHCs have been collected on the resin, the sorbent may require Soxhlet extraction as described above.

3.2 Charcoal (SKC Petroleum-Base or Equivalent)

New charcoal is prepared and charcoal is reconditioned as described in Paragraph 4.4. New charcoal does not require treatment prior to assembly into sorbent cartridges.

3.3 Viton O-Ring

All O-rings used in VOST shall be Viton. Prior to use, these O-rings should be thermally conditioned at 200°C for 48 hours. O-rings should be stored in clean, screw-capped glass containers prior to use.

3.4 Glass Tubes/Condensers

The glass resin tubes and condensers should be cleaned with a non-ionic detergent in an ultrasonic bath, rinsed well with organic-free water, and dried at 110° C.

3.5 Metal Parts

The stainless steel carriers, C-clamps, end plugs, and screens used in the I/0 VOST design are cleaned by ultra sonication in a warm non-ionic detergent solution, rinsed with distilled water, air-dried, and heated in a muffle furnace for 2 hours at 400°C.

3.6 Silica Gel (Indicating Type, 6-16 Mesh)

New silica gel may be used as received.

3.7 Cold Packs

Any commercially available reusable liquids or gels that can be repeatedly frozen are acceptable.

3.8 Water

Water used for cooling train components in the field may be tap water. Water used for rinsing glassware should be organic-free.

3.9 Glass Wool

Glass wool should be Soxhlet extracted for 8 to 16 hours, using methanol, and oven dried at 110°C before use.

4.0 Sample Handling and Procedure

4.1 Assembly

4.1.1 The assembly and packing of the sorbent cartridges should be carried out in an area free of volatile organic material, preferably a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered.

4.2 Tenax® Carbidges

The Tenax®, glass tubes, and metal cartridge parts are cleaned and stored (see Section 3.0). Approximately 1.6 g of Tenax is weighed and packed into the sorbent tube which has a stainless steel screen and C-clamp (I/ 0 design) or glass wool (1/1 design) in the downstream end.

4.3 Tenax® Charcoal Tubes

4.3.1 The Tenax®, charcoal, and metal cartridge parts are cleaned and stored as previously described (see Section 3.0). The tubes are packed with approximately a 3:1 volume ratio of Tenax® and charcoal (approximately 1 g each). The glass tubes containing the Tenax® and charcoal are then conditioned as described below (see Paragraph 4.4).

4.3.2 Glass tubes of the 1/1 design are conditioned and stored in the same manner as the 1/0 tubes.

4.4 Trap Conditioning - QC

4.4.1 Following assembly and leak checking, the traps are connected in reverse direction to sampling to a source of organic-free nitrogen, and nitrogen is passed through each trap at a flow rate of 40 mL/min, while the traps are heated to 190°C for 12 - 28 hours.

4.4.2 The following procedure is used to blank check each set of sampling cartridges prior to sampling to ensure cleanliness. It is not intended as a substitute for Method 5040.

4.4.2.1 The procedure is based on thermal desorption of each set of two cartridges, cryofocusing with liquid nitrogen onto a trap packed with glass beads, followed by thermal desorption from the trap and analysis by GC/FID.

4.4.2.2 The detection limit is based on the analysis of Tenax® cartridges spiked with benzene and toluene and is around 2 ng for each compound.

4.4.2.3 The results of analyzing spiked cartridges on a daily basis should not vary by more than 20 percent.

4.4.2.4 The GC Operating Conditions are as Follows:

Column: Packed column 6 ft x 1/8 in. stainless steel 1.0 percent SP-1000 on Carbopack B 60/80, or equivalent.

Temperature program: 50°C for 5 min, 20°C/min increase to 190°C, hold 13 min.

Injector: 200°C.

Detector: Flame Ionization Detector (FID). 250°C.

Carrier Gas: Helium at 25 mL/min.

Sample valve: Valco 6-port with 40in. X 1/16 in. stainless steel trap packed with 60/80 mesh glass beads.

Cryogen: Liquid nitrogen.

Trap heater: Boiling water, hot oil, or electrically heated.

Desorption heater: Supelco "clam shell" (high capacity carrier gas purifier) heater and Variac, adjusted to 180°C to 200°C.

Calibration is accomplished by preparing a spiked Tenax® cartridge with benzene and toluene and analyzing according to the standard operating procedure

4.4.3 After conditioning, traps are sealed and placed on cold packs until sampling is accomplished.

4.4.4 It may be useful to spike the Tenax® and Tenax®/ charcoal traps with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions.

4.5 Pretest Preparation

4.5.1 All train components shall be cleaned and assembled as previously described. A dry gas meter shall have been calibrated within 30 days prior to use.

4.5.2 The VOST sampling train is assembled. The cartridges should be positioned so that sample flow is through the Tenax® first and then the Tenax®/charcoal.

4.6 Leak Checking

4.6.1 The train is leak checked by closing the valve at the inlet to the first condenser and pulling a vacuum of 250 mm (10 in. Hg) above the normal operating pressure.

4.7 Sample Collection

4.7.1 After leak checking, sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump, and sampling at a rate of 1 L/min for 20 minutes. The volume of sample for any pair of traps should not exceed 20 liters.

4.7.2 Following collection of 20 liters of sample, the train is leak checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax®.

4.7.3 A new pair of cartridges is placed in the VOST, the VOST leak checked, and the sample collection process repeated as described above. Sample collection continues until six pairs of traps have been used.

4.7.4 All sample cartridges should be kept on cold packs until they are ready for analysis.

4.8 Blanks

4.8.1 Field blanks/trip blanks: Blank Tenax® and Tenax® charcoal cartridges are taken to the sampling site and the end caps removed for the period of time required to exchange two pairs of traps on VOST.

4.8.2 Trip Blanks

At least one pair of blank cartridges (one Tenax®, one Tenax®/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site.

4.8.3 Laboratory Blanks

One pair of blank cartridges (one Tenax®, one Tenax®/charcoal) will remain in the laboratory using the method of storage which is used for field samples.

5.0 Calculations (for sample volume)

5.1 Nomenclature used in calculations is foundin Appendix B.

5.2 Volume of Gas Sampled is Calculated:

6.0 Analytical Procedure

See Method 5040.

7.0 Precision and Accuracy Requirements

7.1 Method Performance Check

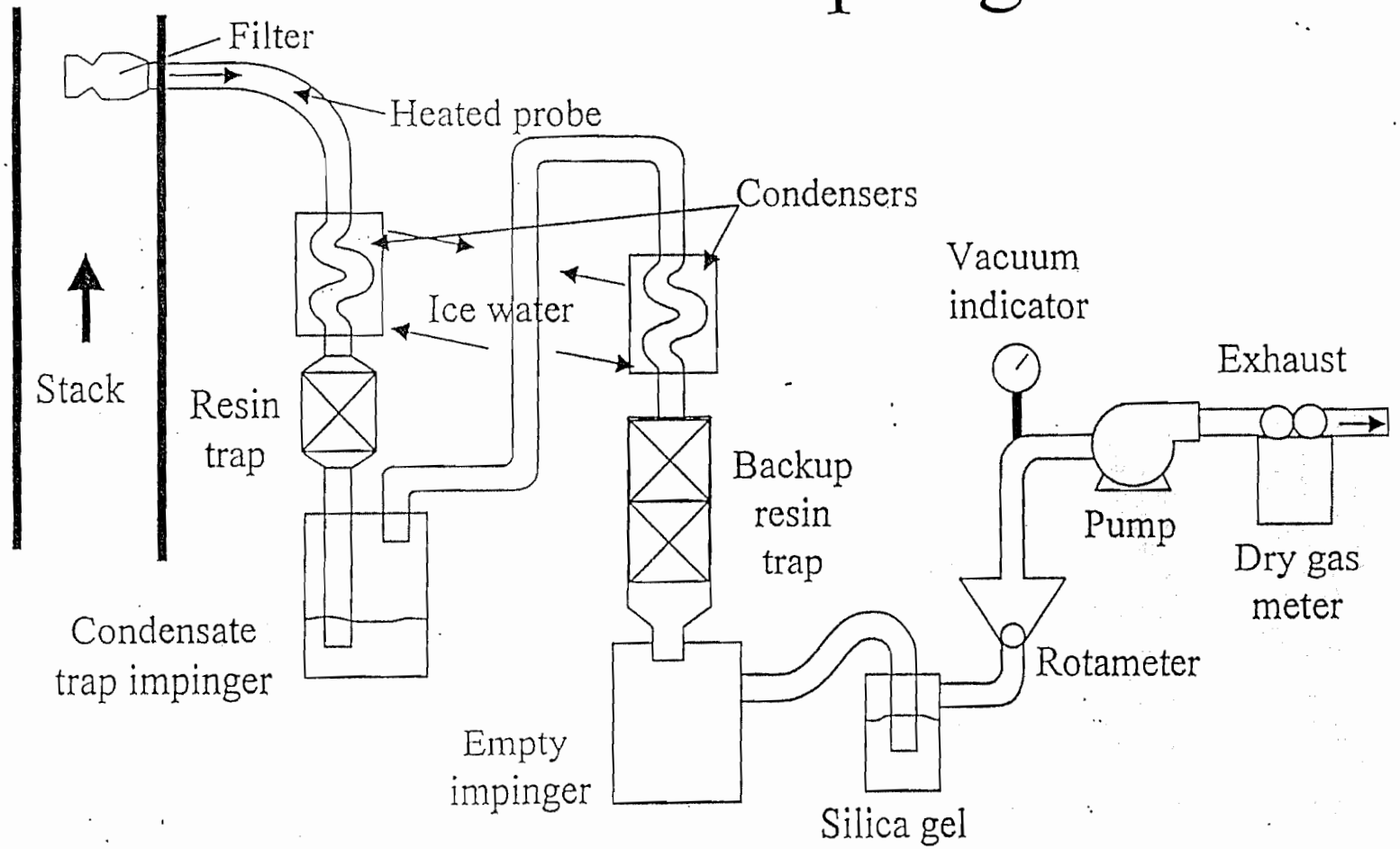
Prior to field operation of the VOST at a hazardous waste incinerator, a method performance check should be conducted using either selected volatile POHCs of interest or two or more of the volatile POHCs for which data are available.

7.2 Performance Audit

During a trial burn a performance audit must be completed. The audit results should agree within 50 to 150 percent of the expected value for each specific target compound.

8.0 References

Method 0030 Sampling Train



SW-846, Method 0031 (ABRIDGED)

Sampling Method for Volatile Organic Compounds (SMVOC)

1.0 Scope and Application

1.1 Method 0031 is used to determine volatile organic compounds in a gaseous state in a wide variety of stationary sources including hazardous waste incinerators.

1.2 Method 0031 may be used to prepare volatile organic compounds that have a boiling point between 15°C and 121°C.

1.3 The method is not applicable to particulates or aerosols since isokinetic sampling is not performed.

1.4 Application of Method 0031 is not restricted to those compounds in the target analyte list; However, detection limits have been determined for these compounds and acceptable method performance data have been obtained.

1.5 Method 0031 is generally not applicable to polar water-soluble and reactive volatile organic compounds.

1.6 This method is applicable to the determination of volatile organic compounds in the gaseous effluent of stationary sources such as hazardous waste incinerators with an upper concentration limit per compound in the emissions of approximately 1.5 parts per million (ppm). Method 0031 is not appropriate for gaseous volatile organic compound concentrations above this limit since saturation of the analytical system or compound breakthrough in the field may occur.

1.7 The sensitivity of this method is dependent upon the level of interferences in the sample matrix and the presence of detectable levels of volatile organic compounds in the blanks.

1.8 The SMVOC is designed to be operated at a sampling rate of 1 L/min with traps being replaced every 20 mm for a total sampling time of 2 hrs.

1.9 This method is restricted to use by, or under close supervision of, trained analytical personnel experienced in sampling volatile organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 This method employs a sampling module and meter box to withdraw a 20 L sample of effluent gas containing volatile organic compounds from a stationary source at a flow rate of 1 L/min, using a glass-lined probe heated to 130 ± 5°C and a sampling method for volatile organic compounds (SMVOC) train.

2.2 The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile organic compounds are collected on a set of sorbent traps (Tenax®-GC/Tenax®-GC/Anasorb®-747). Liquid condensate is collected in an impinger placed between the two Tenax®-GC traps and the Anasorb®-747 trap. The first and second traps contain 1.6 g of Tenax®-GC each and the third trap (back trap) contains 5.0 g of Anasorb®-747.

2.3 Alternative conditions for sample collection may be used.

3.0 Interferences

3.1 Interferences are encountered in the analytical methodology and arise primarily from background contamination of sorbent traps prior to or after sample collection.

3.2 If the emission source has a high level of organic compounds in the emissions matrix (for example, hydrocarbons present at levels of hundreds of ppm), the presence of these volatile organic compounds may interfere with the performance of the SMVOC analytical methodology.

4.0 Apparatus and Materials

4.1 Sampling train - The SMVOC consists of a heated glass-lined probe, followed by an isolation valve and charcoal trap, a water-cooled glass condenser, two sorbent tubes containing Texan®-GC (1.6 ± 0.1 g each), an empty knock-out trap for condensate removal, a second water-cooled glass condenser, a third sorbent tube containing Anasorb®-747 (5.0 g ± 0.1 g), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter.

NOTE. No stainless steel components should be in contact with the sample stream.

4.1.1 Isolation valve - The isolation valve is a greaseless stopcock (0.25 in. outer diameter stem is recommended) with a glass bore and sliding Teflon plug with Teflon washers.

4.1.2 Condensers - The condensers must be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent tube.

4.1.3 Sorbent tubes

4.1.3.1 The first and second tubes of a three-tube set of sorbent tubes should each be packed with 1.6 ± 0.1 g of Tenax®-GC resin and the third tube of the set should be packed with 5.0 ± 0.1 g of Anasorb®-747. The tubes should be marked with an arrow to indicate the direction of flow during sampling.

4.1.3.2 The sorbent tubes are glass tubes with approximate dimensions of 10 cm x 1.6 cm ID.

4.1.3.3 The sorbent tubes are placed in transport tubes (capped culture tubes with glass wool and charcoal) for shipment.

4.1.4 Metering system - The metering system for SMVOC consists of a vacuum gauge, a pump, a calibrated rotameter, a dry gas meter (2% accuracy, with a minimum resolution of 0.01 L at the required sampling rate), needle valves, and a temperature readout device.

4.1.5 Sample transfer lines - All sample transfer lines connecting the probe to the SMVOC shall be less than 1.52 m. (5 ft.) in length.

4.2 Solverall® washers - All washers or gaskets used in SMVOC shall be Teflon®-coated (Solverall® washers or equivalent

4.3 Glass wool - Glass wool shall be Soxhlet-extracted for 8 to 16 hours using methanol, and oven dried at 110°C before use.

4.4 Cold pack/ice - Ice or any commercially-available reusable liquids or gels that can be frozen repeatedly are acceptable.

4.5 VOA vials - 40-mL glass vials with Teflon®-lined screw caps.

4.6 Teflon® squeeze bottles

5.0 Reagents

5.1 Reagent grade inorganic chemicals shall be used in all tests.

5.2 2,6-Diphenyl-p-phenylene oxide polymer (Tenax®-GC, 35/60 mesh, or equivalent).

5.2.1 New Tenax®-GC is Soxhlet-extracted for 24 hours with methanol.

5.2.2 If reuse of Tenax®-GC is necessary, the polymer may be extracted sequentially with methanol and pentane, dried in a vacuum oven, and thermally reconditioned as described above.

5.3 Anasorb®-747 - New Anasorb®-747 is used as it is received from the manufacturer without preparation other than thermal conditioning pending a Quality Control check (Sec. 7.1.1).

5.4 Silica gel - Indicating type, 6-16 mesh.

5.5 Methanol, CH_3OH - The methanol used for extracting the Tenax®-GC and glass wool should be pesticide grade or equivalent.

5.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

6.0 Sample Collection, Preservation, and Handling

6.1 SMVOC glassware cleaning. All glass components of the train should be cleaned thoroughly.

6.1.1 Sonicate for 1 hour in a solution of a laboratory detergent such as Alconox®.

6.1.2 Rinse with copious amounts of hot tap water to remove all detergent residue.

6.1.3 Rinse three times with HPLC grade water.

6.1.4 Oven dry at 110°C.

6.1.5 Cap for shipment using Teflon® tape or aluminum foil.

6.2 Assembly

The assembly and packing of the sorbent tubes should be carried out in a laboratory in which no organic solvents are stored and in which the laboratory air is charcoal filtered. Alternatively, a glove box is suggested.

6.3 Tenax®-GC tubes

6.3.1 The Tenax®-GC glass tubes and metal tube parts are cleaned and stored (see Sec. 6.1).

6.3.2 Conditioned sorbent tubes are capped and placed on cold packs or ice for storage and transport.

6.4 Anasorb®-747 tubes - Anasorb-747 (5.0 ± 0.1 g) is weighed and packed into the third sorbent tube which also has unsilanized cleaned glass wool in the downstream end.

6.5 Sample collection

6.5.1 For sample collection, place the inlet of the probe at the centroid of the stack or at a point no closer to the wall than 1 meter. After leak checking (see Sec. 6.5.3) but before the initiation of sample collection, the probe shall be purged with stack gas.

6.5.2 Sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump, and sampling at a rate of 1 L/min (or slower rate, if desired, according to the guidelines for SLO-SMVOC) for 20 minutes (or an appropriately longer period, if slower sampling rates are used).

6.5.3 Following completion of sample collection, the SMVOC is leak checked a second time at the highest vacuum encountered during the sampling run to minimize the chance of vacuum desorption of volatile organic compounds from Tenax® GC.

6.5.4 Depending upon condensate volume collected, recovery may be performed with each tube change, or at the end of each run (nominally 2 hrs).

6.5.5 A new set of tubes is placed in the SMVOC, the SMVOC is leak checked, and the sample collection process repeated as described above.

6.6 Blanks

6.6.1 Field blanks - Blank Tenax®-GC and Anasorb®-747 tubes are attached to the sampling train while the train is leak checked.

6.6.2 Trip blanks - At least one set of blank tubes (two Tenax®-GC, one Anasorb®-747) should be included with each shipment of tubes to a stationary source sampling site.

6.6.3 Laboratory blanks - One set of blank tubes (two Tenax®-GC, one Anasorb®-747) should remain in the laboratory using the method of storage which is used for field samples.

7.0 Procedure

7.1 Tube conditioning

7.1.1 In a desorption oven, the sorbent tubes are connected to a source of organic-free nitrogen. Nitrogen is passed through each tube at a flow rate of 80-100 mL/min while the tubes are heated.

7.1.2 An acceptable blank level is less than or equal to Method Detection Limits for Method 5041/8280 (see Method 8260 for Method Detection Limits).

7.1.3 After conditioning, tubes are sealed and placed on cold packs or ice (maintained at a temperature less than 10 °C) until sampling is completed.

7.2 Pretest preparation

7.2.1 All train components should be cleaned and assembled as previously described.

7.2.2 The SMVOC is assembled. Cooling water should be circulated to the condensers and the temperature of the cooling water must be low enough to maintain the temperature of the gas entering the sorbent below 20°C.

7.3 Leak checking

7.3.1 To leak check the entire train, it is necessary to leak check from the probe to the pump.

7.3.2 Ensure that all connections are tight and that the train is assembled correctly with sorbent cartridges properly assembled and in the right direction for sampling.

7.3.3 Upon completion of the leak check, turn off the pump and release the pressure/vacuum in the train by turning the isolation valve to the vacuum release position and allowing ambient air (filtered with charcoal or equivalent) to enter the train.

7.4 Sample collection - Sample collection procedures are described in Sec. 6.5.

7.5 Analytical procedure - Samples are analyzed by Methods 5041 and 8260.

7.4 Calculations

8.0 Quality Control

8.1 Prior to actual sampling on-site, all of the applicable sampling equipment should be thoroughly checked to ensure that each component is clean and operable. Each of the equipment calibration data forms should be reviewed for completeness and adequacy to ensure the acceptability of the equipment.

8.2 The following quality control (QC) checks are applicable to the sampling procedures.

8.2.1 Each sampling train must be visually inspected for proper assembly before every use.

8.2.2 All sampling data should be recorded on standard data forms.

8.2.3 The temperature measurement system should be visually checked for damage and

operability by measuring the ambient temperature.

8.2.4 All sampling data and calculations should be recorded on pre-formatted data sheets.

8.2.5 All glassware for SMVOC should be cleaned.

8.2.6 Ten percent of the SMVOC tubes should be subjected to GC/MS QC measurements.

8.2.7 All cleaned glassware, hardware, and prepared sorbent traps should be kept closed with ground-glass caps or Teflon® tape until assembly of the sampling train in the field.

8.2.8 Prior to sampling, the Tenax®-GC and Anasorb®-747 tubes should be spiked with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions.

8.2.9 Assembly and recovery of the sampling trains must be performed in an environment as free from uncontrolled dust and solvent vapors as possible.

8.2.10 Blanks (field, trip, laboratory) must be collected.

8.2.11 The entire sampling train should be leak checked before and after each run.

8.2.12 Dry gas meter readings, temperature readings, and pump vacuum readings should be made during sampling and recorded in intervals no greater than 5 minutes.

8.2.13 Sorbent traps should be used for sampling within two weeks of preparation.

8.2.14 During sample collection, the gas stream temperature at the inlet to the first sorbent trap must be maintained at or below 20^0C.

8.2.15 All sample traps should be stored under refrigeration or on ice or cold packs.

8.3 QC for analytical procedures

8.3.1 Calibration standards should be prepared at five different concentration levels for each analyte of interest.

8.3.2 To establish the precision and accuracy of the analysis, triplicate paired Tenax®-GC tubes should be spiked with analytical surrogate volatile organic compounds using flash evaporation and analyzed immediately following the initial calibration and before sample analysis.

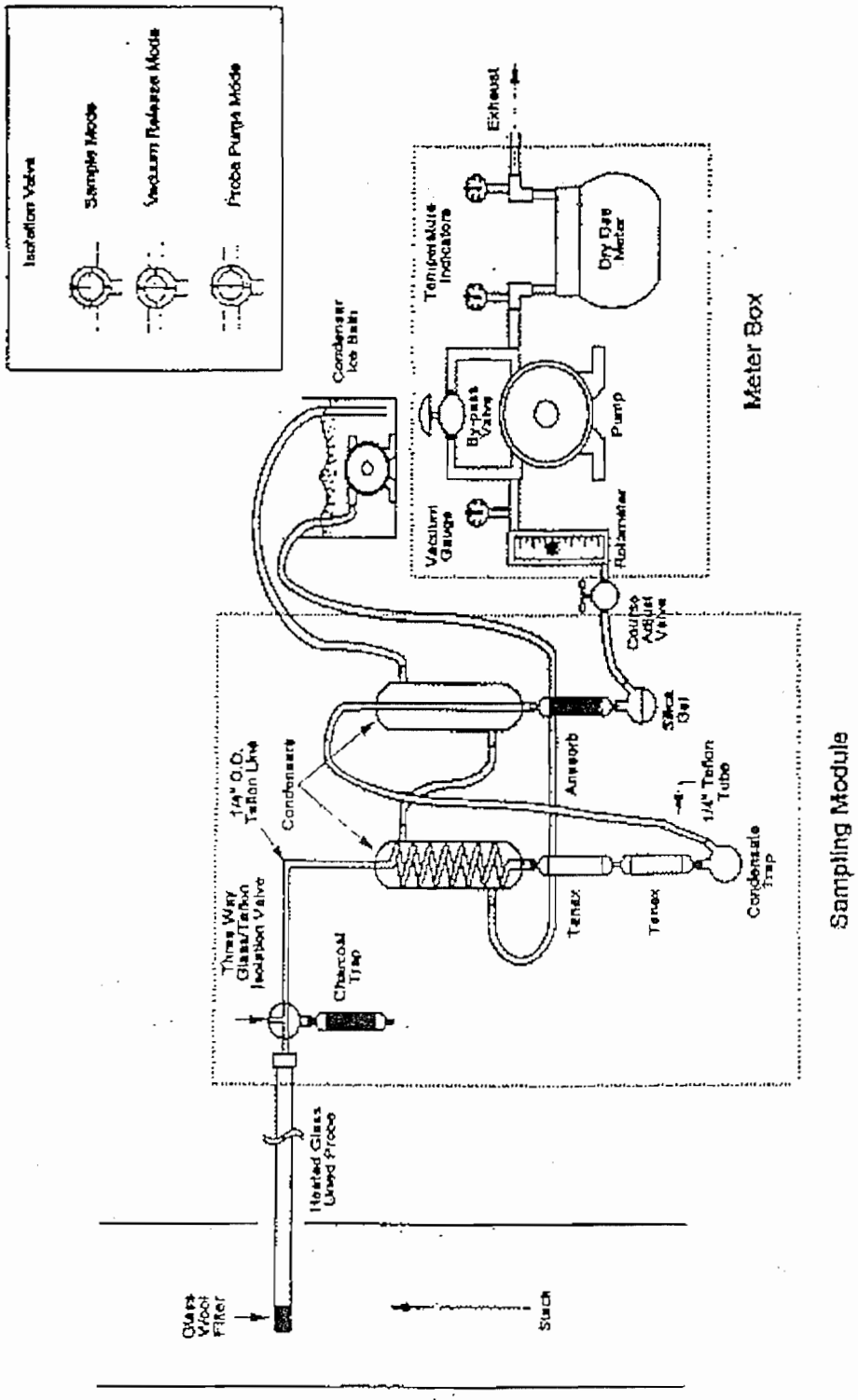
8.3.3 The average recovery from the initial precision and accuracy determinations should be used as an acceptance criterion for sample results.

8.3.4 An EPA performance audit should be completed during a trial rum as a check on the entire SMVOC system.

9.0 Method Performance

See Method 8260.

10.0 References


Isolation Valve
Sample Mode
Vacuum Release Mode
Probe Pump Mode
Exhaust
Temperature Indicators
Dry Gas Meter
Condenser Ice Bath
Bypass Valve
Pump
Vacuum Gauge
Rotameter
Meter Box
Coarse Adjust Valve
Silica Gel
Condensate
1/4" O.D. Teflon Line
Three Way Glass/Teflon Isolation Valve
Charcoal Trap
Tenax
Tenax
1/4" Teflon Tube
Condensate Trap
Sampling Module
Heated Glass Lined Probe
Glass Wool Filter
Stack

SW-846, Method 0050 (ABRIDGED)

Determination of Hydrogen Chloride Emissions from Stationary Sources (Isokinetic)

1.0 Scope and Application

1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in-stack gas emission samples from hazardous waste incinerators and municipal waste combustors. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., HCl dissolved in water droplets).

A midget impinger train sampling method designed for sampling sources of HCl/Cl_2 emissions not in particulate form is presented in Method 0051. The method has potential for collection of all halogens and halogen acids, but has not yet been fully evaluated for that use. For analytical determination of additional halides, Method 9056 is used, rather than Method 9057.

1.2 This method is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm.

1.3 This method may also be used to collect samples for subsequent determination of particulate emissions (Method 5, see Ref. 1) following the additional sampling procedures described.

2.0 Summary of Method

2.1 Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain liquid droplets. The Teflon mat or quartz-fiber filter collects other particulate matter including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl_2, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl_2 dissolved in the liquid in the cyclone and/or on the filter is vaporized to gas and ultimately collected in the impingers by pulling Ascarite IIR conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl^-) ions. The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO). The (Cl^-) ions in the separate solutions are measured by ion chromatography (Method 9057). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

The stoichiometry of HCl and Cl_2 collection in the sampling train is described in this section.

3.0 Interferences

3.1 Volatile materials that produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present.

4.0 Apparatus and Materials

4.1 Sampling Train.

4.1.1 The sampling train configuration is adapted from Method 5 and Method 0010 procedures. The majority of the required equipment is identical to that used in Method 0010 determinations. The new components required are a glass nozzle and probe, a Teflon union, a quartz-fiber or Teflon mat filter (see Section 5.5), a Teflon frit, and acidic and alkaline absorbing solutions.

4.1.2 Construction details for the basic train components are provided in Section 3.4 of EPA's *Quality Assurance Handbook*, Volume III; commercial models of this equipment are also available. Additionally, the following subsections identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are also described in the U. S. Environmental Protection Agency, Publication No. EPA-600/4-77-027b, August 1977. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle

Glass with sharp, tapered (30° angle) leading edge. In cases where the stack temperature exceeds 210°C (410°F), a one-piece glass nozzle/liner assembly must be used. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated according to the procedures outlined in Method 5.

4.1.3.2 Probe liner

Borosilicate or quartz-glass tubing with a heated system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F) at the exit end during sampling. 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 1650°F). Water cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

4.1.3.3 Pitot tube

Type S, as described in Method 2. The Type-S pitot tube assembly shall have a known coefficient.

4.1.3.4 Differential pressure gauge

Inclined manometer or equivalent device as described in Method 2. One manometer shall be used for velocity head (Δp) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Cyclone (optional)

Borosilicate glass.

4.1.3.6 Filter holder

Borosilicate glass, with a Teflon frit filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials.

4.1.3.7 Filter heating system

Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) around the filter holder and cyclone during sampling. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

4.1.3.8 Impinger train

The following system shall be used to determine the stack gas moisture content and to collect HCl and Cl_2:

Five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings.

The first impinger (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under test conditions which require such a trap, and should contain 50 mL of 0.05 M H_2SO_4.

The following two impingers (acid impingers, each containing 100 mL of 0.05 M H_2SO_4), shall be of the Greenburg-Smith design with the standard tip (see Method 0010, Section 4).

The next two impingers (alkaline impingers each contain 100 mL of 0.1 M NaOH)

The last impinger (containing silica gel) shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (0.51 in.) I.D. glass tube extending about 1.3 cm from the bottom of the impinger (see Method 5).

4.1.3.9 Metering system

The necessary components are a 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 1%, an orifice meter (rate meter), and related equipment.

4.1.3.10 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). The barometric reading may be obtained from a nearby National Weather Service station.

4.1.3.11 Gas density determination equipment

Temperature sensor and pressure gauge (as described in Method 2), and gas analyzer, if necessary (as described in Method 3, Reference 1). The temperature sensor ideally should 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.

4.1.3.12 Ascarite tube for conditioning ambient air

Tube tightly packed with approximately 150 g of fresh 8 to 20-mesh Ascarite IIR sodium hydroxide coated silica, or equivalent.

4.2 Sample Recovery.

4.2.1 Probe liner

Probe and nozzle brushes; nylon (Teflon) bristle brushes with stainless steel wire handles are required. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.

4.2.2 Wash bottles

Two. Polyethylene or glass, 500 mL or larger.

4.2.3 Glass sample storage containers

Glass, 500 or 1,000 mL. Screw-cap liners shall be Teflon and constructed so as to be leak-free.

4.2.4 Petri dishes

Glass or plastic sealed around the circumference with Teflon tape.

4.2.5 Graduated cylinder and/or balances

To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balance capable of weighing to ± 0.5 g or better is required.

4.2.6 Plastic storage containers

Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 Funnel and rubber policeman

To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 Funnels

Glass, to aid in sample recovery.

5.0 Reagents

5.1 Reagent grade inorganic chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.

5.2 Reagent water - All references to water in the method refer to reagent grade water as defined in Chapter One unless otherwise specified.

5.3 Sulfuric acid (0.05 M), H_2SO_4 - Used as the HCl absorbing reagent in the impinger train.

5.4 Sodium hydroxide (0. 1 M), NaOH - Used as the Cl_2 absorbing reagent in the impinger train.

5.5 Filter - Quartz-fiber or Teflon mat filter, or equivalent.

5.6 Silica gel - Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours before using.

5.7 Acetone - When using this train for determination of particulate emissions, reagent grade acetone, 0.001 percent residue, in glass bottles is required.

5.8 Crushed ice - Quantities ranging from 10-50 lbs may be necessary during a sampling run, depending on ambient air temperature.

5.9 Screw-on connectors - Teflon sleeves on ground-glass joints, or other greaseless fittings should be used.

5.10 Sodium thiosulfate (0.5 M), $Na_2S_2O_3$ - Used as the reducing agent added to the sodium hydroxide filled impingers to promote the reaction given in Section 2.0.

6.0 Sample Collection, Preservation, and Handling

6.1 Sample collection is described in this method. The analytical procedures for HCl

and Cl_2 are described in Method 9057 and for particulate matter in Method 0100.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis.

7.0 Procedure

7.1 Preparation for Field Test.

7.1.1 All sampling equipment shall be maintained and calibrated according to procedures described in Section 3.4.2 of EPA's *Quality Assurance Handbook*, Volume III and in Methods 1-5.

7.1.2 Weigh several 200-300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers.

7.1.3 Check filters visually against light for irregularities and flaws or pinhole leaks.

7.1.4 If a particulate determination will be conducted, desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hours. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2-3 hours, desiccated for 2 hours, and weighed.

7.2 Preliminary Field Determinations.

7.2.1 Select the sampling site and the minimum number of sampling points according to Method 1. Determine the stack pressure, temperature, and range of velocity heads using Method 2. It is recommended that a leak check of the pitot lines (see Method 2) be performed. Determine the stack gas moisture content using Method 4 or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3. 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 sample run.

7.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size to maintain isokinetic sampling rates.

7.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled.

7.2.4 The total sampling time should be two hours. Allocate the same time to all traverse points defined by Method 1.

7.3 Preparation of Sampling Train.

7.3.1 Add 50 mL of 0.05 M H_2SO_4 to the condensate impinger, if used. Place 100 mL of 0.05 M H_2SO_4 in each of the next two impingers. Place 100 mL of 0.1 M NaOH in each of the following two impingers. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last impinger.

7.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) filter (weighed, if particulate matter is to be determined) in the filter holder. Check the filter for tears after assembly is completed.

7.3.3 To use glass liners, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass fiber gasket when temperatures are higher.

7.3.4 Set up the train. Connect temperature sensors to the appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

7.3.5 Place crushed ice around the impingers.

7.3.6 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

7.4 Leak Check Procedures.

7.4.1 Pretest leak check. A pretest leak check is recommended, but not required. The following procedure shall be used.

7.4.1.1 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 by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

7.4.1.2 If a woven glass fiber gasket is used, first plug the inlet to the cyclone, (if used), or the filter holder and pull a 380 mm Hg (15 in. Hg) vacuum. Then, connect the probe to the train and leak check at about 25 mm Hg (1 in. Hg) vacuum.

7.4.1.3 The leak check instructions in this section may be helpful.

7.4.1.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, cyclone, or filter holder and immediately turn off the vacuum pump.

7.4.2 Leak checks during sample run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary or a port change is conducted, a leak check shall be conducted immediately after the interruption of sampling and before the change is made.

7.4.3 Post-test leak check. A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done using the same procedures as those with the pretest leak check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run.

7.5 Train Operation.

7.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic. Maintain a temperature around the filter and (cyclone, if used) of 120 ± 14 °C (248 ± 25°F).

7.5.2 For each run, record the data required on a data sheet. 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 at least once at each sample point during each time.

7.5.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are positioned properly.

7.5.4 When the stack is under significant negative pressure (equivalent to the height of the 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.

7.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

7.5.6 Traverse the stack cross section, as required by Method 1, being careful not to bump the probe nozzle into the stack walls.

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

7.5.8 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, it may be replaced in the midst of a sample run.

7.5.9 If the condensate impinger becomes too full, it may be emptied, recharged with 50 mL of 0.05 M H_2SO_4,and replaced during the sample run.

7.5.10 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.

7.5.11 Note that when two or more trains are used, separate analyses of the particulate catch (if applicable) and the HCl and Cl_2 impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains.

7.5.12 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, and record the final dry gas meter reading.

7.5.13 If there is any possibility that liquid has collected in the glass cyclone and/or on the filter, connect the Ascarite tube at the probe inlet and operate the train with the filter heating system at 120 ± 14°C (248 ± 25°F) at a low flow rate (e.g., $\Delta H = 1$) sufficient to vaporize the liquid and purge any HCl in the cyclone or on the filter and pull it through the train into the impingers.

7.5.14 Conduct a post-test leak check. Also, leak check the pitot lines as described in Method 2. The lines must pass this leak check in order to validate the velocity head data.

7.5.15 If the moisture value is available, calculate percent isokineticity (see Section 7.7.10) to determine whether the run was valid or another test run should be conducted.

7.6 Sample Recovery.

7.6.1 Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap over the tip.

7.6.2 Before moving the sampling train to the cleanup site, remove the probe and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Cap the filter holder outlet and the impinger inlet.

7.6.3 Transfer the probe and filter/impinger assembly to the cleanup area.

7.6.4 Save portions of all washing solutions used for cleanup (acetone and reagent grade water) and the absorbing reagents (0.05 M H_2SO_4 and 0.1 M NaOH) as blanks. Transfer 200 mL of each solution directly from the wash bottle being used (rinse solutions) or the supply container (absorbing reagents) and place each in a separate, pre-labeled glass sample container.

7.6.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.6.6 Container No. 1 (filter catch for particulate determination). Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Label the container and seal with Teflon tape around the circumference of the lid.

7.6.7 Container No. 2 (front half rinse for particulate determination). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone into a glass container. Retain an acetone blank and analyze with the samples.

7.6.8 Perform 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.

7.6.9 Have two people 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 solvent.

7.6.10 Follow the acetone rinse with a probe brush. Hold the probe in an inclined position and squirt acetone into the upper end while pushing the probe brush through the probe with a twisting action. Run the brush through the probe until no visible particulate matter is carried out with the acetone or none remains in the probe liner on visual inspection.

7.6.11 Clean the inside of the front half of the filter holder and cyclone by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Label the container to identify its contents.

7.6.12 Container No. 3 (knockout and acid impinger catch for moisture and HCl determination). Disconnect the impingers. Measure the liquid in the acid and knockout 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. Rinse these impingers and the connecting glassware (and tubing, if used) with water, and add these rinses to the storage container. Seal the container, shake to mix, and label.

7.6.13 Container No. 4 (alkaline impinger catch for Cl_2 and moisture determination). Measure and record the liquid in the alkaline impingers as described in Section 7.6.12. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 2 mL or more of 0.5 M $Na_2S_2O_3$, to the sodium hydroxide (NaOH) samples.

7.6.14 Container No. 5 (silica gel for moisture determination). 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 last impinger to its original container and seal.

7.6.15 Prior to shipment, recheck all sample containers to ensure that the caps are well secured.

7.7 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.7.1 Nomenclature.

7.7.2 Average dry gas meter temperature and average orifice pressure drop.

7.7.3 Dry gas volume. Correct the sample measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)].

7.7.4 Volume of water vapor.

7.7.5 Moisture content.

7.7.6 Acetone blank concentration. For particulate determination.

7.7.7 Acetone wash blank. For particulate determination.

7.7.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from Container Nos. 1 and 2 less the acetone blank (W_a).

7.7.9 Particulate concentration.

7.7.10 Isokinetic variation.

7.7.10.1 Calculation from raw data.

7.7.10.2 Calculation for intermediate values.

7.7.11 Acceptable results. If 90% < I < 110%, the results are acceptable.

7.7.12 Analytical calculation for total pg HCl per sample.

7.7.13 Analytical calculation for total pg Cl_2 per sample.

7.7.14 Concentration of HCl in the flue gas.

8.0 Quality Control

8.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

8.2 Analysis. At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

8.3 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Institute of Standards and Technology (SRM 3182).

8.4 Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

9.0 Method Performance

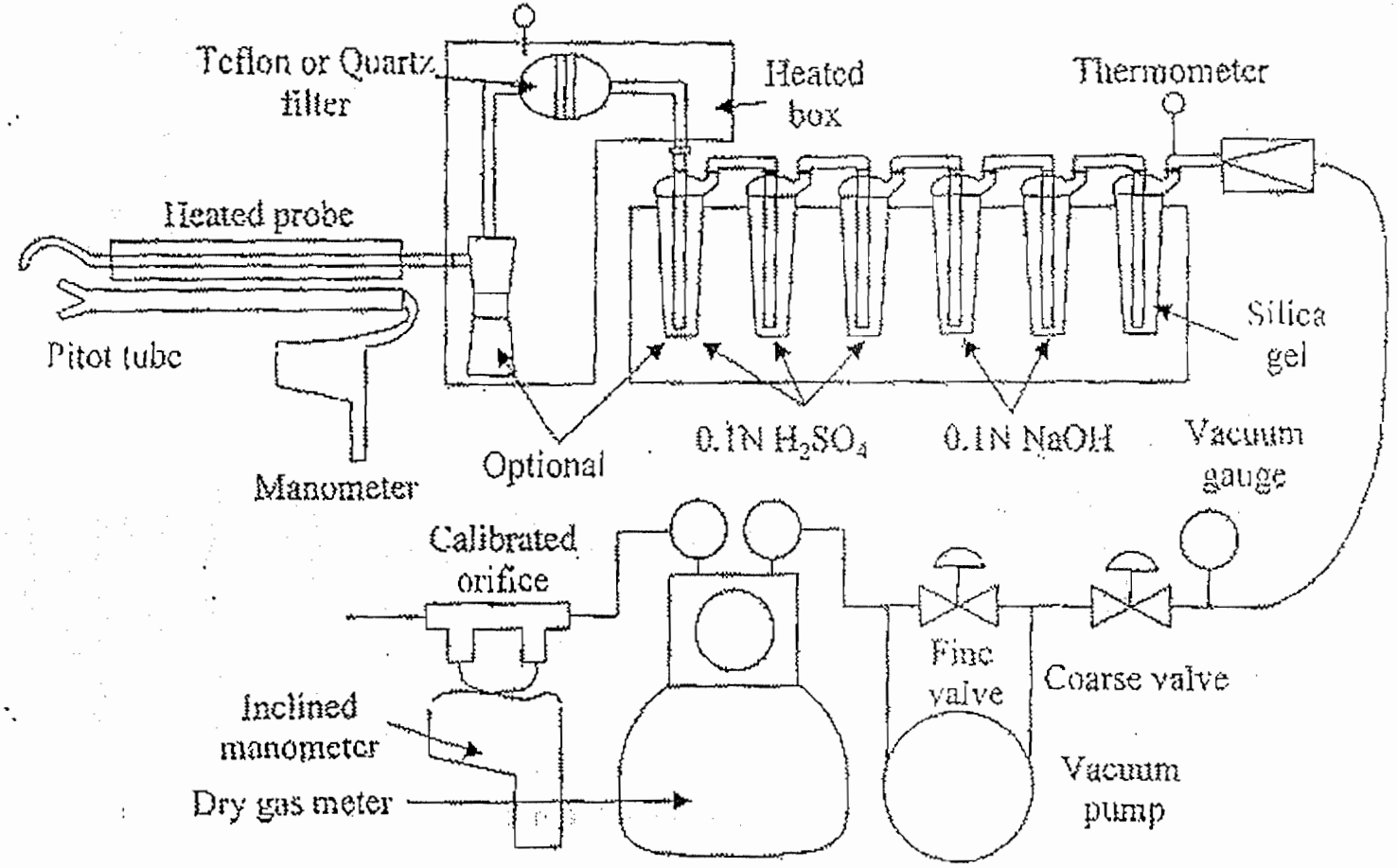
9.1 The in-stack limit for HCl for the method is approximately 0.02 mg/dscm of stack gas. The method has a negative bias below 20 ppm HCl (Reference 6).

9.2 It is preferable to include the cyclone in the sampling train to protect the filter from any moisture present.

9.3 The lower detection limit of the analytical method is 0. 1 μg of Cl^- per mL of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

9.4 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl_2 train (Method 0051) for sample collection. The laboratory relative standard deviation is within 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

Method 0050 Sampling Train



SW-846, Method 0051 (ABRIDGED)

Determination of Hydrogen Chloride Emissions from Stationary Sources (Midget Impinger)

1.0 Scope and Application

This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method 9057. This method is designed to collect HCl/CL_2 in their gaseous forms. Use of this method is limited to the sampling of relatively dry, particulate-free gas streams. Sources controlled by wet scrubbers, that emit acid particulate matter must be sampled using an isokinetic HCl/Cl_2 sampling train (see Method 0050). This method has potential for collection of all halogens and halogen acids, but has not been fully evaluated for that use. For analytical determination of additional halides, Method 9056 is used rather than Method 9057.

2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts that could potentially react and form the analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) as follows:

$$HCl + H_2O = H_3O+ Cl^-$$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

The Cl^- ions in the separate solutions are measured by ion chromatography (Method 9057).

Sodium thiosulfate solution is added to the contents of the hydroxide filled impingers.

Conversion of all the original Cl_2 to the stable Cl^- ion, and appropriate adjustment of the analysis calculations, removes the possibility of partial reduction of OCl^- to Cl^- and the resulting high bias to the results.

3.0 Interferences

Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

4.0 Apparatus and Materials

4.1 Sampling Train: The sampling train and component parts are discussed below.

4.1.1 Probe: Borosilicate glass, approximately 3/8-in. (9-mm) I.D., with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in. (9-mm) I.D. Teflon elbow should be attached to the inlet of the probe. A 1-in. (25-mm) length of Teflon tubing with a 3/8 in. (9-mm) I.D. should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the gas stream, thus reducing the amount of particulate entering the train. Where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool plug be used to remove particulate matter, use of such a filtering device could result in a bias in the data. Instead, a Teflon

filter should be used as specified in Section 5.5.

4.1.2 Three-way stopcock: A borosilicate, three-way glass stopcock with a heating system to prevent condensation.

4.1.3 Impingers: Five 30-mL midget impingers with leak-free glass connectors.

4.1.4 Mae West impinger or drying tube: Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

4.1.5 Sample line: Leak-free, with compatible fittings to connect the last impinger to the needle valve.

4.1.6 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0. 1 in. Hg). Reading may be obtained from a nearby National Weather Service station.

4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter: Pump capable of purging sample probe at 2 L/min with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 L/min.

4.1.8 Metering system: The following items comprise the metering system, which is identical to that used for EPA Method 6.

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

4.1.8.2 Pump: Leak-free diaphragm pump, or equivalent, to pull gas through train.

4.1.8.3 Rate meter: Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 L/min.

4.1.8.4 Volume meter: Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent.

4.1.8.5 Vacuum gauge: At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

4.1.9 Water Bath: To minimize loss of absorbing solution.

4.2 Sample Recovery.

4.2.1 Wash bottles: Two, polyethylene or glass, 500 mL or larger.

4.2.2 Storage bottles: Glass, with Teflon-lined lids, 100 mL, to store impinger samples (two per sampling run).

5.0 Reagents

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.

5.2 Reagent Water: All references to water in the method refer to reagent water as defined in Chapter One unless otherwise specified.

5.3 Sulfuric acid (0.05 M), H_2SO_4: Used as the HCl absorbing reagent.

5.4 Sodium hydroxide (0.1 M), NaOH: Used as the Cl_2 absorbing reagent.

5.5 Filter: Teflon mat Pallflex TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250°F.

5.6 Sodium Thiosulfate (0.5 M), $Na_2S_2O_3$: Used as the reducing agent added to the sodium hydroxide filled impingers to promote the reaction given in Section 2.0.

5.7 Silica gel. Indicating type, 6 to 16-mesh. 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.

6.0 Sample Collection, Preservation, and Handling

6.1 Sample collection is described in this method. The analytical procedures are described in Method 9057.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 Procedure

7.1 Calibration. Section 3.5.2 of EPA's *Quality Assurance Handbook,* Volume III may be used as a guide for these operations.

7.1.1 Dry Gas Metering System.

7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system. 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, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results.

7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in Section 7.1.1.1 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, (c) only two independent runs need to be made. If the calibration factor does no deviate by more than 5 percent from the initial calibration factor (determined in Section 7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable.

7.1.2 Thermometer(s): Prior to each field test, calibrate against mercury-in-glass thermometer at ambient temperature. If the thermometer being calibrated reads within 2°C (3.6°F) of the mercury-in-glass thermometer, it is acceptable.

7.1.3 Rate meter: The rate meter should be cleaned and maintained according to the manufacturer's instructions.

7.1.4 Barometer: Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer.

7.2 Sampling.

7.2.1 Preparation of collection train: Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 mL of 0.05 M H_2SO_4. The fourth and fifth impingers should each be filled with 15 mL of 0.1 M NaOH. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel.

7.2.2 Leak check procedures: Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided.

7.2.3 Purge procedures: Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe. Turn on the purge pump, and adjust the purge rate to 2 L/min. Purge for at least 5 minutes prior to sampling.

7.2.4 Sample collection: Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train. Adjust the sampling rate to 2 L/min as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 7.2.2.

7.3 Sample recovery: Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. Then, disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.05 M H_2SO_4 impingers) to a leak-free storage bottle.

7.4 Calculations: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.4.1 Nomenclature.

7.4.2 Calculate sample volume, dry basis, corrected to standard conditions.

7.4.3 Calculate volume of water vapor.

7.4.4 Calculate moisture content.

7.4.5 Calculate total µg HCl per sample.

7.4.6 Calculate total µg Cl_2 per sample.

7.4.7 Calculate concentration of HCl in the flue gas.

8.0 Quality Control

8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

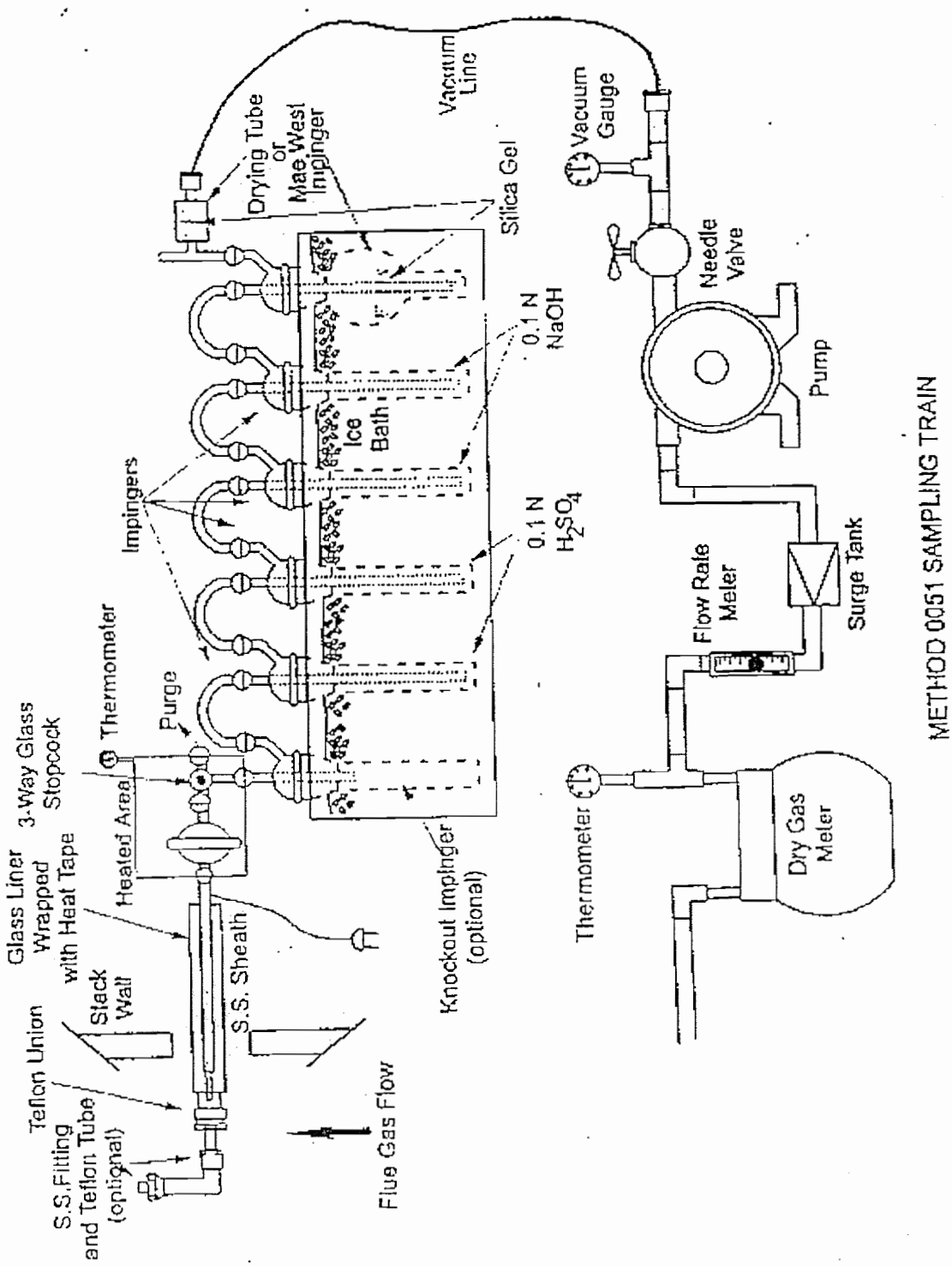
8.2 Quality control check sample.

9.0 Method Performance

9.1 The in-stack limit for HCl for the method is approximately 0.08 mg/dscm of stack gas for a 1hour sample.

9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol, Method 9057, have been determined. The laboratory relative standard deviation is within 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

10.0 References



METHOD 0051 SAMPLING TRAIN

W-846, Method 0060
ABRIDGED)

etermination of Metals in Stack missions

.0 Scope and Application

This method is used to determine the concentration of metals in stack emissions from hazardous waste incinerators and similar combustion processes.

.1 This method may also be used for the determination of particulate emissions following the additional procedures described in Section 7.1.5.2.

.2 For the analyses described in this methodology and for similar analyses, the response for Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is linear over several orders of magnitude. Samples containing metal concentrations in the micrograms per liter (pg/L) to milligrams per liter (mg/L) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 mg/L of chromium, lead, or arsenic or greater than approximately 20 mg/L of cadmium should be diluted to that level or lower for final analysis.

.3 The actual method detection limits are sample dependent and may vary as the sample matrix affects the limits. Method detection limits for antimony can also be dependent on the digestion method used and may be considerably higher than the estimated detection limits. Method detection limits for all analytes may differ from the estimated detection limits when hydrofluoric acid digestion is used.

1.4 The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced, and knowledgeable, in handling and preparing reagents, and in using adequate safety procedures and protective equipment.

2.0 Summary

2.1 The stack sample is withdrawn isokinetically from the source. Particulate emissions are collected in the probe and on a heated filter and gaseous emissions are collected in a series of chilled impingers. Two impingers are empty, two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide, two other impingers contain acidic potassium permanganate solution, and the last impinger contains a desiccant.

2.2 Sampling components are recovered and digested in separate front half and back half fractions. Materials collected in the sampling train are acid digested to dissolve inorganics and to remove organic constituents that may create analytical interferences.

2.3 The nitric acid and hydrogen peroxide impinger solution, the hydrochloric acid rinse solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by Cold Vapor Atomic Absorption Spectrometry (CVAA).

Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FLAA), or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. If greater analytical sensitivity than can be obtained by ICP-AES is required, then Graphite Furnace Atomic Absorption Spectrometry (GFAA) is used for the analysis.

2.4 For convenience, aliquots of each digested sample Fraction 1A, as described in Section 7.2.3.2, plus Fraction 2A, as described in Section 7.2.4, can be combined for a single analytical determination, proportionally with respect to the original Fractions 1 A and 2A.

2.5 The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals as described in Section 8.0 of this method including actual sample matrix effects checks.

3.0 Interferences

3.1 Refer to the appropriate determinative method for instructions on minimization of interferences.

4.0 Apparatus and Materials

4.1 Sampling train - Is similar to the Method 5 train. The sampling train consists of the following components.

quantity of liquid involved, the tester may place the impinger solutions from Impingers 1, 2, and 3 in more than one container.

5 Containers No. 5A (0.1M HNO), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8M HCl rinse and dilution). If mercury is not being measured in this train, then Impingers 4, 5, and 6 are not necessary and may be eliminated.

5.1 Pour all the liquid, if any, from the impinger which was empty at the start of the run (normally Impinger 4) and which precedes the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 mL. NOTE: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle. These bottles shall not be filled full and shall be vented to relieve excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner is suggested.

5.2 If no visible deposits remain after the above described water rinse, do not rinse with HCl.

Container No. 6 (silica gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal.

Container No. 7 (acetone blank). If particulate emissions are to be determined, at least once during each field test, place 100 mL portion of the acetone used in the sample recovery process into a labeled container for use in the front half field reagent blank. Seal the container.

Container No. 8A (0.1 M nitric acid blank). At least once during each field test, place 300 mL of the 0.1 M nitric acid solution used in the sample recovery process into a labeled container for use in the sample recovery.

Container No. 8B (water blank). At least once during each field test, place 100 mL of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

7.1.5.10 Container No. 9 (5 percent nitric acid/10 percent hydrogen peroxide blank). At least once during each field test, place 200 mL of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

7.1.5.11 Container No. 10 (acidified potassium permanganate blank). At least once during each field test, place 100 mL of the acidified potassium permanganate solution used as the impinger solution into a labeled container for use in the back half field reagent blank for mercury analysis. Prepare the container as described in Section 7.2.5.5.1 note.

7.1.5.12 Container No. 11 (8M HCl blank). At least once during each field test, place 200 mL of water into a sample container. Then pour 25 mL of 8M HCl carefully with stirring into the 200 mL of water in the container. Mix well and seal the container.

7.1.5.13 Container No. 12 (filter blank). Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. This will be used in the front half field reagent blank.

7.2 Sample preparation. Note the level of the liquid in each of the containers and confirm on the analysis sheet whether or not leakage occurred during transport.

7.2.1 Container No. 1 (filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5.

NOTE: Hydrofluoric acid (HF) has been identified as an exceptional health and contact hazard.

7.2.2 Container No. 2 (acetone rinse). Measure the liquid in this container either volumetrically to +1 mL or gravimetrically to +0.5 g.

7.2.3 Container No. 3 (probe rinse). The pH of this sample shall be 2 or lower.

7.2.3.1 Digest the sample using the appropriate method (Method 3010, 3015, or Parr Bomb),

7.2.3.2 Combine with the digestate prepared in Section 7.2.1. The resultant combined sample is a Fraction 1 precursor.

7.2.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL.

7.2.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other.

7.2.5.1 Measure and record the volumes of 5A and 5B each to within 0.5 mL.

7.2.5.2 Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small.

7.2.6 Container No. 6 (silica gel). 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).

7.3 Calibration

Refer to the appropriate analytical methods for the proper calibration procedures.

7.4 Sample analysis.

7.4.1 For each sampling train, seven individual samples are generated for analysis.

7.4.2 The back half of the train was used to prepare the third through seventh samples.

7.4.3 Samples 5A, 5B, and 5C are labeled Fractions 3A, 3B, and 3C, respectively. They consist of the impinger contents and rinses from the empty Impinger 4 and the permanganate Impingers 5 and 6.

7.4.4 Initially, analyze all samples for iron, aluminum, and all the target metals except mercury.

NOTE: Since all front half samples will contain hydrofluoric acid, use an alumina torch.

7.4.5 ICP-AES analysis. Fraction 1A and Fraction 2A are analyzed by ICP-AES using Method 6010.

7.4.6 AA by direct aspiration and/or graphite furnace.

7.4.7 Cold vapor AA mercury analysis. Fraction 1 B, Fraction 213, and Fraction 3A, 313, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectrometry following the method outlined in Method 7470.

7.4.8 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. Refer to Method 6020 for the proper analytical procedure.

7.5 Calculations

7.5.1 Dry gas volume. Calculate $Vm_{(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

7.5.2 Volume of water vapor and moisture content. Calculate the volume of water vapor $Vw_{(std)}$ and the moisture content Bws of the stack gas.

7.5.3 Stack gas velocity. Using Equation 2-9 of Method 2, calculate the average stack gas velocity.

7.5.4 Metals (except mercury) in source sample.

7.5.4.1 Fraction 1A, front half, metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train.

7.5.4.2 Fraction 2A, back-half, metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train.

7.5.4.3 Total train, metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling.

7.5.5 Mercury in source sample.

7.5.5.1 Fraction 1B, front half, Hg. Calculate the amount of mercury collected in the fron-half, Fraction 1, of the sampling train.

7.5.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, back half, Hg. Calculate the amount of mercury collected in Fraction 2, 3A, 313, and 3C. Calculate the total amount of mercury collected in the back-half of the sampling train.

7.5.5.3 Total train mercury catch. Calculate the total amount of mercury collected in the sampling train.

7.5.6 Metal concentration of stack gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, cobalt, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions).

7.5.7 Isokinetic variation and acceptable results. Same as Method 5, Sections 6.11 and 6.12, respectively.

8.0 QUALITY CONTROL

8.1 Sampling Blanks.

8.2 Quality Control Samples.

8.2.1 ICP-AES or ICP-MS analysis.

8.2.2 Direct aspiration and/or graphite furnace AA analysis for antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc.

8.2.3 Cold vapor AA analysis for mercury.

9.0 METHOD PERFORMANCE

9.1 To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits.

9.2 Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above.

1. A 1 hour sampling run collects a stack gas sampling volume of about 1.25 M^3.

2. The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 mL for the front half (Fraction 1) and 150 mL for the back half (Fraction 2A).

3. When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative.

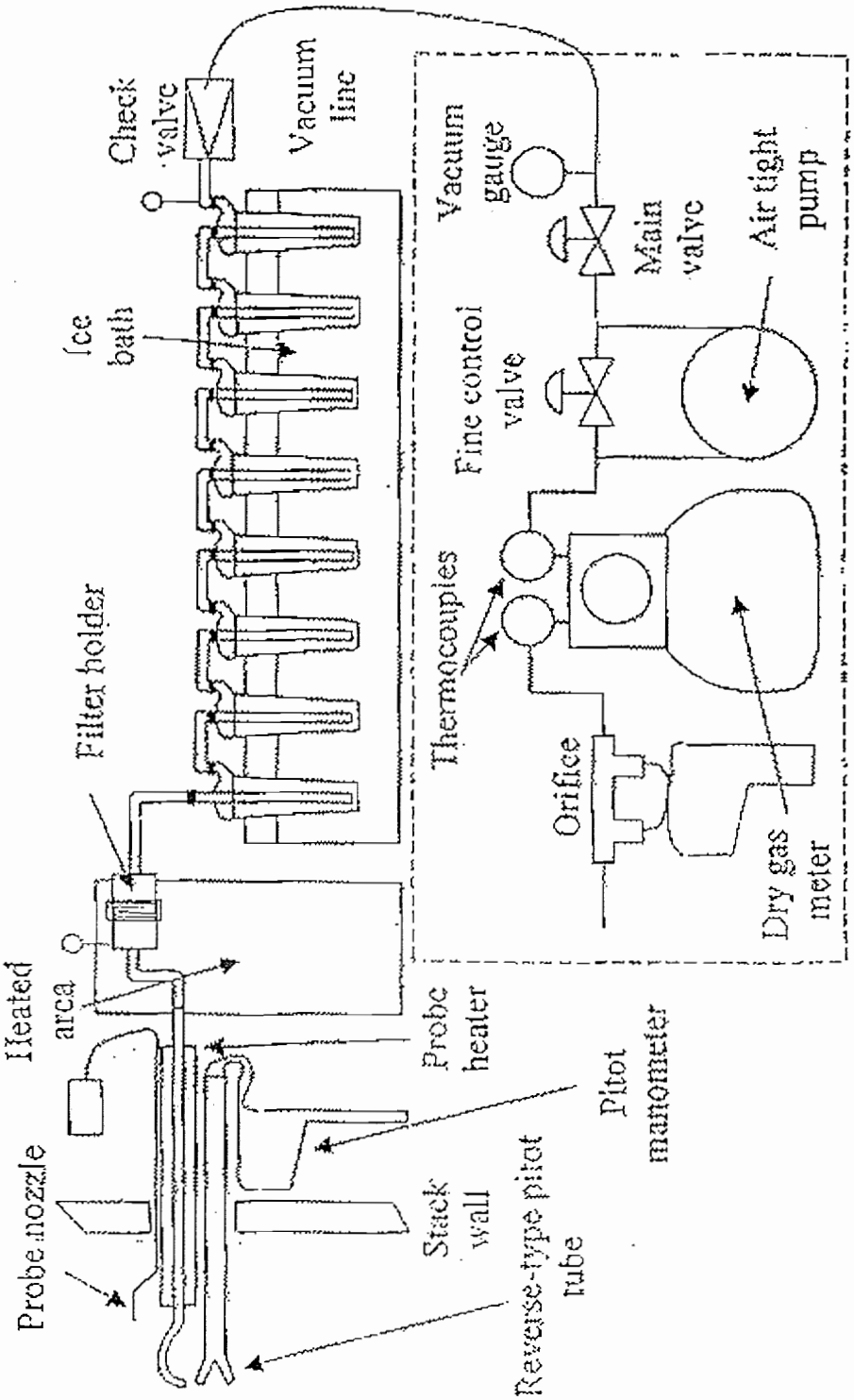
4. Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase detection limits (i.e., the method would be less sensitive).

5. The above discussion assumes no blank correction.

Using (1) the procedures described in this method, (2) the analytical detection limits listed in Section 1, (3) a volume of 300 mL for the front half and 150-mL for the back half samples, and (4) a stack gas sample volume of 1.25 M^3, the corresponding in-stack method detection may be calculated.

10.0 REFERENCES

Method 0060 Sampling Train



SW-846, Method 0061 (ABRIDGED)

Determination of Hexavalent Chromium Emissions From Stationary Sources

1.0 Scope and Application

1.1 This method provides procedures for the determination of hexavalent chromium (Cr^{+6}) emissions from hazardous waste incinerators, municipal waste incinerators, municipal waste combustors, and sewage sludge incinerators. The sampling train, constructed of Teflon components, has only been evaluated at temperatures of less than 300°F. Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.

1.2 Range: If employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in solution). With sample dilution, there is no upper limit. Follow your manufacturer's specific instructions on employing the preconcentration procedure for these analyses.

2.0 Summary of Method

2.1 For incinerators and combustors, the Cr^{+6} emissions are collected isokinetically from the source. To eliminate the possibility of Cr^{+6} reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for Cr^{+6} by an ion chromatograph equipped with a post-column reactor (PCR) and a visible wavelength detector. The IC/PCR separates the Cr^{+6} as chromate (CrO_4^{-2}) from other diphenylcarbazide reactions that occur in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system may also be used in conjunction with the IC/PCR.

3.0 Interferences

3.1 Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6}. A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences.

3.2 The chromatographic separation of Cr^{+6} using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause interference.

3.3 Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be obtained by increasing the injection volume of the samples to ten times the size of the sample loop.

4.0 Apparatus

4.1 Sampling Train: The sampling system uses a recirculatory sampling train to capture Cr^{+6}. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon. The metering system is identical to that specified by Method 5; the sampling train consists of the following components.

4.1.1 Probe Nozzle: Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be < 30 degrees and the taper should be outside to perserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated.

4.1.2 Teflon Aspirator or Pump/Sprayer Assembly: Teflon aspirator capable of recirculating absorbing reagent at 50 mL/min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator.

4.1.3 Teflon Sample Line: Teflon, 3/8 in. I.D., of suitable length to connect aspirator (or T-union) to first Teflon impinger.

4.1.4 Teflon Recirculation Line: Teflon, 1/4 in. O.D. and 1/8 in. I.D., of suitable length to connect first impinger to aspirator (or T-union).

4.1.5 Teflon Impingers: Four Teflon impingers; Teflon tubes and fittings, such as made by Savillex*, can be used to connect impingers 2 in. diameter by 12 in. long, with vacuum-tight 3/8 in. O.D. Teflon compression fittings. The second and third 3/8 in. O.D. Teflon stem has a 1/4 in. O.D. Teflon tube, 2 in. long, inserted at its impinger stem should extend to 2 in. from impinger bottom, high enough in the impinger reagent to prevent air from entering recirculating line. The second and third impinger stems should extend to 1/2 in. from impinger bottom. The first impinger should include a 1/4 in. O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger to trap solution carried over from the previous impingers.

4.1.6 Glass Impinger: Silica gel impinger, Vacuum-tight impingers, capable of containing 400 g of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (0.5 in. I.D. at tip of stem).

4.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

4.1.8 Metering System, Barometer, and Gas Density Determinations Equipment: Same as Method 0010.

4.2 Sample Recovery: Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinsing thoroughly with reagent water before use.

4.2.1 Nitrogen Purge Line: Inert tubing and fittings capable of delivering 0 to 1 scf/min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder.

4.2.2 Wash Bottles: Two polyethylene wash bottles, for reagent water-nitric rinse solution.

4.2.3 Sample Storage Containers: Polyethylene, with leak-free screw cap, 500 mL or 1000 mL.

4.2.4 1000 mL Graduated Cylinder and Balance.

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

4.2.6 Funnel and Rubber Policeman: To aid in transfer of silica gel from impinger to storage container.

4.3 Sample Preparation for Analysis: Sample preparation prior to analysis includes purging the sample train immediately following the sample run, and filtering the recovered sample to remove particulate matter immediately following recovery.

4.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders: Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards.

4.3.2 Filtration Apparatus: Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

4.4 Ion Chromatograph: Refer to Section 4.0 of SW-846, Method 7199 for instrument and equipment specifications.

4.4.1 Preconcentrator: System in-line with the ion chromatograph.

4.5 Sample preconcentration system: A high performance ion chromatograph (HPIC) non-metallic column with acceptable anion retention characteristics and sample loading rates as described in the analytical method.

5.0 Reagents

5.1 All inorganic reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

5.2 Sampling.

5.2.1 Reagent water shall be interferences free. All references to water in the method refer to reagent water unless otherwise specified.

5.2.2 Potassium Hydroxide, 0.1 M: Add 5.6 g of KOH to approximately 900 mL of reagent water and let dissolve. Dilute to 1000 mL with reagent water.

NOTE: Sources with high concentrations of acids and/or SO_2, the concentration of KOH should be increased to 0.5 M to ensure that

the pH of the solution is above 8.5 after sampling.

5.2.3 Silica Gel and Crushed Ice: Same as Method 5.

5.3 Sample Recovery.

5.3.1 Water: Same as Section 5.2.1.

5.3.2 Nitric Acid, 0.1 M: Add 6.3 mL of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 mL of reagent water. Dilute to 1000 mL with reagent water, and mix well.

5.3.3 pH Indicator Strip: pH indicator capable of determining pH of solution between the pH range of 7 and 12, at 0.5 pH intervals.

5.4 Sample Preparation

5.4.1 Reagent water: Same as Section 5.2.1.

5.4.2 Nitric Acid, 0.1 M: Same as Section 5.3.2.

5.4.3 Filters: Acetate membrane, or equivalent, filters with 0.45 μm or smaller pore size.

5.5 Analysis

5.5.1 Refer to Section 5.0 of Method 7199 for instruction on preparation of analytical reagents.

5.6 Performance Audit Sample: A performance audit sample should be analyzed in conjunction with the samples.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Section 6.0 of Method 7199 for the proper procedures when collecting, preserving, and handling samples.

6.2 If sample preconcentration is used, dropwise addition of the ammonium sulfate/ammonium hydroxide buffer may not be appropriate, since the added sulfate may lead to premature overloading of the column.

6.3 A holding time of 14 days is appropriate for samples collected by Method 0061, even though Method 7199 has a 24 hr hold for other samples. The Method 0061 samples are already stabilized in an alkaline solution, as opposed to many samples from other media which may be submitted for analysis in an unstable condition.

7.0 Procedure

CAUTION: Wear safety glasses at all times during this test method.

7.1 Sampling: Testers should be trained and experienced with test procedures.

7.1.1 Sample Train Calibration: Calibrate the sample train components according to the indicated sections of Method 5.

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

7.1.3 Preliminary Determinations: Same as Method 5.

7.1.4 Preparation of Sampling Train: Measure 300 mL of 0.1 M KOH into a graduated cylinder (or tare-weighed, precleaned polyethylene container). Place approximately 140 mL of the 0.1 M KOH reagent in the first Teflon impinger. Split the rest of the 0.1 M KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a pre-weighed 200 to 400 g portion of indicating silica gel in the final glass impinger.

7.1.5 Leak Check Procedures: Follow the leak check procedures given in Method 5.

7.1.6 Sampling Train Operation: Follow the procedures given in Method 5, Section 4.1.5.

NOTE: If the gas to be sampled is above 200°F, it may be necessary to wrap three or four feet of the Teflon sample and recirculating lines inside the ice bath to keep the recirculated reagent cool enough so it does not turn to steam.

For each run, record the data required on a data sheet.

7.1.7 Calculation of Percent Isokinetic: Same as Method 5, Section 4.

7.2 Post-test Nitrogen Purge: The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state.

7.3 Sample Recovery: Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run.

7.3.1 Container No. 1 (Impingers 1 through 3): Disconnect the first impinger from the

second impinger and disconnect the recirculation line from the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighted precleaned polyethylene sample container and measure the volume of the liquid to within 1 mL or 1 g Record the volume of liquid present.

7.3.2 Container No. 2 (HNO_3 rinse optional for total chromium).

7.3.3 Container No. 3 (Silica Gel): Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container and seal the container.

7.3.4 Container No 4 (0.1 M KOH Blank): Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container.

7.3.5 Container No. 5 (Reagent Water Blank): Once during each field test, place a volume of reagent water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container.

7.3.6 Container No. 6 (0.1 M HNO_3 Blank): Once during each field test if total chromium is to be determined, place a volume of 0.1 M HNO_3 reagent equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container.

Sample Preparation: For determination of Cr^{+6}, the sample should be filtered immediately following recovery to remove any insoluble matter.

7.3.7 Container No. 2 (HNO_3 rinse, optional for total chromium): This sample shall be analyzed in accordance with the selected procedure for total chromium analysis.

7.3.8 Container 3 (Silica Gel): Weigh the spent silica gel to the nearest 0.5 g using a balance.

7.4 Sample Analysis: The Cr^{+6} content of the sample filtrate is determined by ion chromatography coupled with a post column reactor (IC/PCR). Method 7199 should be used for this analysis.

7.4.1 Preconcentration: The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent, followed by removal of the analyte from the absorbent.

Refer to Section 7.0 of Method 7199 for the proper sample analysis protocol.

7.5 Calculations

7.5.1 Dry Gas Volume: Calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Method 5.

7.5.2 Volume of Water Vapor and Moisture Content: Calculate $V_{w(std)}$ and B_{ws}, the volume of water vapor and the moisture content of the stack gas, respectively, using equations in Method 5.

7.5.3 Stack Gas Velocity: Use equations in Method 2 to calculate the average stack gas velocity.

7.5.4 Calculate total μg Cr^{+6} per sample.

8.0 Quality Control

9.0 Method Performance

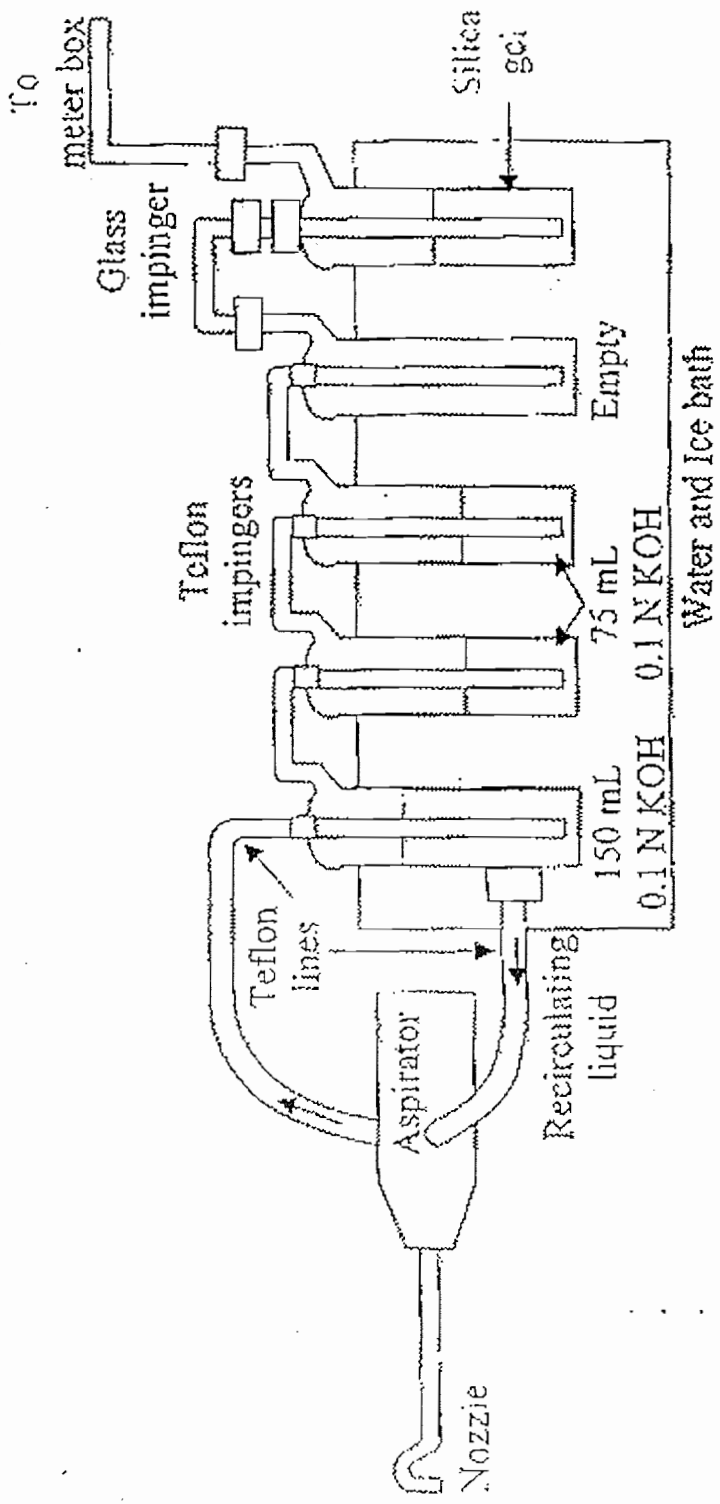
9.1 Sensitivity: A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution). Follow instrument manufacturers instructions for sample preconcentration.

9.2 Precision: The precision of the IC/PCR with sample preconcentration is 5 to 10%. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 μg/dscm of total chromium is 25% and 9% for Cr^{+6} and total chromium, respectively. For hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6}, it is 20%.

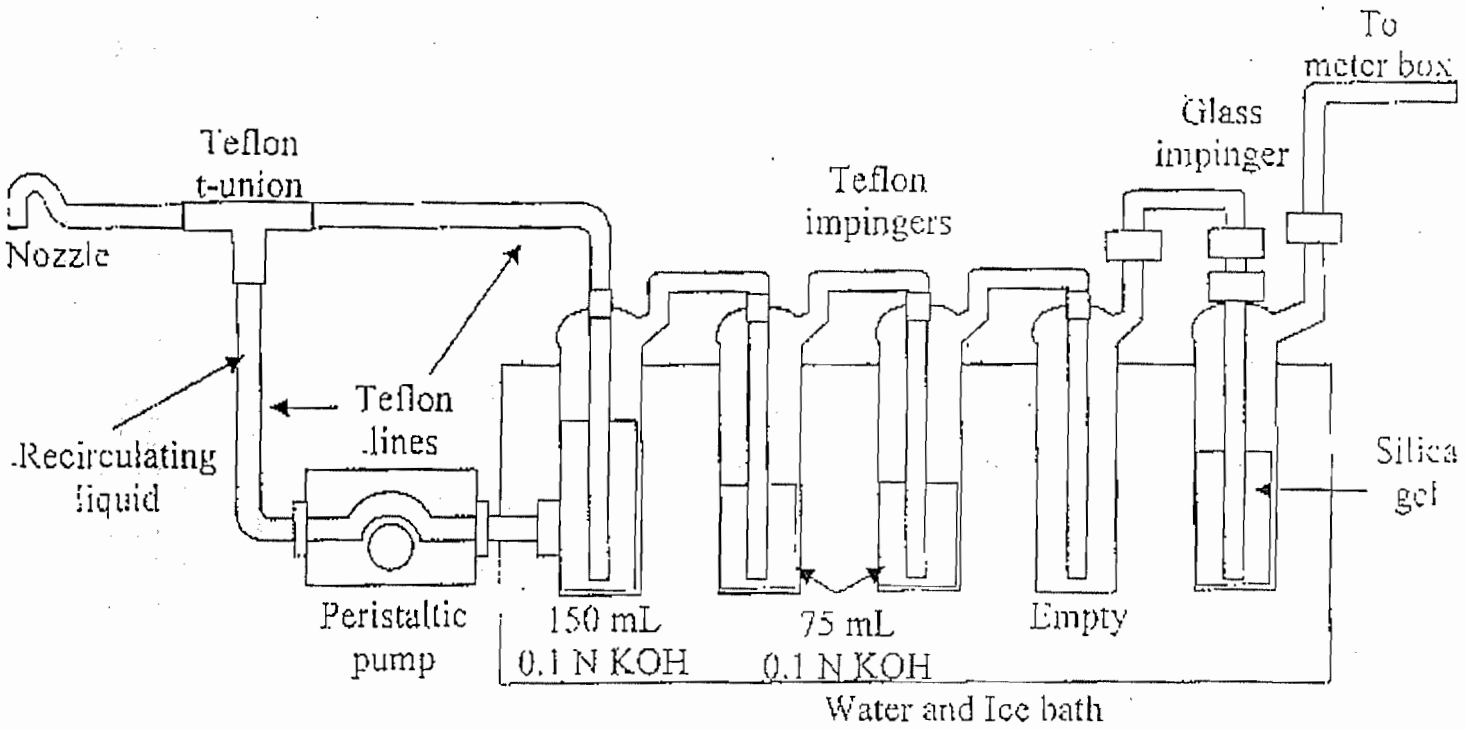
9.3 Refer to Method 7199 for additional analytical method performance information.

10.0 References

Method 0061 Sampling Train



Method 0061 Sampling Train



Appendix A

Equations

General

$$\Delta H = K(\Delta p)$$

$$\overline{pmr}_s = c_s Q_s$$

$$A_s = \pi\left(\frac{D_s}{2}\right)^2$$

$$A_s = LW$$

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

$$\%EA = \frac{(\%O_2) + 0.5(\%CO)}{0.0264(\%N_2) - (\%O_2) + 0.5(\%CO)}$$

$$\%N_2 = 100 - \%CO_2 - \%O_2 - \%CO$$

Method 1

Equation 1-1

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

Equation 1-2

$$R_i = \arccos ine[(\cos ineY_i)(\cos ineP_i)]$$

Equation 1-3

$$\overline{R} = \frac{\sum R_i}{n}$$

Equation 1-4

$$S_d = \sqrt{\frac{\sum_{i=1}^{n}(R_i - \overline{R})^2}{(n-1)}}$$

Method 2

Equation 2-1

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

Equation 2-2

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

Equation 2-3

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

Equation 2-4

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

Equation 2-5

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

Equation 2-6

$$= P_{bar} + P_g$$

Equation 2-7

$= 273 + t_s$ for metric.

Equation 2-8

$= 460 + t_s$ for English.

Equation 2-9

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

Equation 2-10

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

Method 2F

Equation 2F-1

$$F_1 = \frac{(P_4 - P_5)}{(P_1 - P_2)}$$

Equation 2F-2

$$F_2 = C_p \sqrt{\frac{\Delta p_{std}}{(P_1 - P_2)}}$$

Equation 2F-3

$$\% \, Diff = \frac{F_2^{\max} - F_2^{\min}}{F_2^{\min}} \, x \, 100\%$$

Equation 2F-4

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

Equation 2F-5

$$P_s = P_{bar} + \frac{P_g}{13.6}$$

Equation 2F-6

$$T_{s(i)} = 273 + t_{s(i)}$$

Equation 2F-7

$$T_{s(i)} = 460 + t_{s(i)}$$

Equation 2F-8

$$v_{a(i)} = K_p \, F_{2(i)} \sqrt{\frac{(P_1 - P_2)_i \, T_{s(i)}}{P_s \, M_s}} (\cos\theta_{y(i)}) (\cos\theta_{p(i)})$$

Equation 2F-9

$$v_{a(avg)} = \frac{\sum_{i=1}^{n} v_{a(i)}}{n}$$

Equation 2F-10

$$Q_{sw} = 3{,}600(v_{a(avg)})(A)\left(\frac{T_{std}}{T_{s(avg)}}\right)\left(\frac{P_s}{P_{std}}\right)$$

Equation 2F-11

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

Method 3

Equation 3-1

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

Method 3A

Equation 3A-1

$$C_{gas} = \frac{C_{ma} - C_{oa}}{C_m - C_o}(\overline{C} - C_m) + C_{ma}$$

Method 4

Equation 4-1

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w RT_{std}}{P_{std} M_w} = K_1 (V_f - V_i)$$

Equation 4-2

$$V_{wsg(std)} = \frac{(W_f - W_i)RT_{std}}{P_{std} M_w} = K_2 (W_f - W_i)$$

Equation 4-3

$$V_{m(std)} = V_m Y \frac{(P_m)(T_{std})}{(P_{std})(T_m)} = K_3 Y \frac{V_m P_m}{T_m}$$

Equation 4-4

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

Equation 4-5

$$V_{wc} = \frac{(V_f - V_i)\rho_w RT_{std}}{P_{std} M_w} = K_1 (V_f - V_i)$$

Equation 4-6

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right) = K_2 \frac{V_m P_m}{T_m}$$

Equation 4-7

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

Method 5

Equation 5-9a

$$\Delta H_{@} = 0.0319\,\Delta H \frac{T_m}{P_{bar}} \frac{\theta^2}{Y^2 V^2{}_m}$$

Equation 5-1

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

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

Equation 5-1a

$$\left[V_m - (L_p - L_a)\right]$$

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

Equation 5-2

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

$$= K_2\, V_{lc}$$

Equation 5-3

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

Equation 5-4

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

Equation 5-5

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

Equation 5-6

$$c_s = (0.001\ g/mg)\left(\frac{m_n}{V_{m(std)}}\right)$$

Equation 5-7

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

Equation 5-8

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

$$= \frac{K_4\, T_s\, V_{m(std)}}{P_s\, v_s\, A_n\, \theta\, (1 - B_{ws})}$$

Equation 5-8a

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

Equation 5-9

$$K' = \frac{K_1\, V_m\, Y\left(P_{bar} + \frac{\Delta H}{13.6}\right)\sqrt{T_{amb}}}{P_{bar}\, T_m\, \theta}$$

Equation 5-10

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

Equation 5-11

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

Equation 5-12

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

Method 6

Equation 6-1

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

Equation 6-2

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

Equation 6-3

$$RE = \frac{C_d - C_a}{C_a}(100)$$

Equation 6-4

$$V_{sb(std)} = V_{sb} \left(\frac{T_{std}}{T_{amb}}\right)\left(\frac{P_{bar}}{P_{std}}\right)$$

Equation 6-5

$$Q_{std} = \frac{V_{sb(std)}}{\theta}$$

Equation 6-6

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

Equation 6-7

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

Method 6A

Equation 6A-1

$$V_{CO2(std)} = 5.467\, x 10^{-4}\, (m_{af} - m_{ai})$$

Equation 6A-2

$$V_{w(std)} = 1.336\, x 10^{-3}\, (m_{wf} - m_{wi})$$

Equation 6A-3

$$C_{SO_2} = 32.03 \frac{(V_t - V_{tb})\, N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)} + V_{CO_2(std)}}$$

Equation 6A-4

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_{m(std)} + V_{CO_2(std)}} x 100$$

Equation 6A-5

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{CO2(std)}}$$

Equation 6A-7

$$m_{SO_2} = 32.03 (V_t - V_{tb}) N \left(\frac{V_{soln}}{V_s} \right)$$

Equation 6A-8

$$E_{SO_2} = F_c \, (1.829 x 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})}$$

Method 6C

Equation 6C-1

$$C_{gas} = (\overline{C} - C_o) \frac{C_{ma}}{C_m - C_o}$$

Method 7

Equation 7-1

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

Equation 7-2

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

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

Equation 7-3

$$m = 2 K_c \, A \, F$$

Equation 7-4

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

Equation 7-5

$$RE = \frac{C_d - C_a}{C_a} (100)$$

Method 8

Equation 8-1

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

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

Equation 8-2

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

Equation 8-3

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

Equation 8-4

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

Equation 8-5

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

Method 11

Equation 11-1

$$N_s = 2.039 \frac{W}{V_s}$$

Equation 11-2

$$N_A = 0.2039 \frac{W}{V_s}$$

Equation 11-3

$$N_I = N_T \frac{V_T}{V_I}$$

Equation 11-4

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

Equation 11-5

$$C_{H2S} = \frac{K \left[(V_{IT} N_I - V_{TT} N_T) sample - (V_{IT} N_I - V_{TT} N_T) \right]}{V_{m(std)}}$$

Method 15

Equation 15-1

$$C = \frac{(K)(P_r)}{ML}$$

Equation 15-2

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

Equation 15-3

$$Average \ SO_2 \ equivalent = \frac{\sum_{i=1}^{N} SO_2 \ equiv_i}{N}$$

Method 15A

Equation 15A-1

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

Equation 15A-2

$$V_{mc(std)} = \frac{k_1 Y_c (V_{mc})(P_{bar})}{T_m}$$

Equation 15A-3

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

Equation 15A-4

$$C_{RG} = \frac{(C_{COS})(Q_{COS})}{Q_{COS} + Q_{N2}}$$

Equation 15A-5

$$R = \frac{C_{TRS}}{C_{RG}} x100$$

Method 16

Equation 16-1

$$C = K \frac{P_r}{ML}$$

Equation 16-2

$$TRS = \sum (H_2S, MeSH, DMS, 2DMDS)\, d$$

Equation 16-3

$$AverageTRS = \frac{\sum_{i=1}^{N} TRS_i}{N(1 - B_{WO})}$$

Equation 16-4

$$C = \frac{\sum_{i=1}^{N} S_i}{N}$$

Method 16A

Equation 16A-1

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

Equation 16A-2

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

Equation 16A-3

$$C_{RG} = \frac{(Q_{H2S})(C_{H2S})}{Q_{H2S} + Q_{CG}}$$

Equation 16A-4

$$R = \frac{C_{TRS}}{C_{RG}} x100$$

Equation 16A-5

$$N_T = \frac{1}{ml\ Na_2 S_2 O_3\ Consumed}$$

Equation 16A-6

$$N_1 = \frac{N_T V_T}{V_1}$$

Equation 16A-7

$$V_{m(std)} = (\bar{Q}_{std})(\theta_s)(1 - B_{wa})\frac{M_a}{M_b}$$

Equation 16A-8

$$C_{H2S} = \frac{K N_T (V_{TB} - V_T)}{V_{m(std)}}$$

Method 16B

Equation 16B-1

$$C_{TRS} = (C_{SO2})(d)$$

Equation 16B-2

$$C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N}$$

Method 18

Equation 18-1

$$C_s = \frac{10^6 (\bar{x} q_c)}{q_c + q_d}$$

Equation 18-2

$$C_s = 106\bar{x}\left(\frac{q_{c1}}{q_{c1} + q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2} + q_{d2}}\right)$$

Equation 18-3

$$C_s = \frac{G_V x10^6 \frac{293}{T_s}\frac{P_s}{760}}{V_m Y \frac{293}{T_m}\frac{P_m}{760}1000} = \frac{G_V x10^3 \frac{P_s}{T_s}\frac{T_m}{P_m}}{V_m Y}$$

Equation 18-4

$$C_s = \frac{\frac{L_V}{M}\rho(24.055x10^6)}{V_m Y \frac{293}{T_m}\frac{P_m}{760}1000} = 6.24x10^4 \frac{L_V \rho T_m}{M V_m Y P_m}$$

Equation 18-5

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r (1 - B_{ws})}$$

Method 20

Equation 20-1

$$C_d = \frac{C_w}{1 - B_{ws}}$$

Equation 20-2

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

Equation 20-3

$$X_{CO2} = \frac{5.9}{F_o}$$

Equation 20-4

$$C_{adj} = C_d \frac{5.9}{20.0 - \%O_2}$$

Equation 20-5

$$C_{adj} = C_d \frac{X_{CO2}}{\%CO_2}$$

Equation 20-6

$$E = C_d F_d \frac{20.9}{20.9 - \%O_2}$$

Equation 20-7

$$E = C_d F_c \frac{100}{\%CO_2}$$

Equation 20-8

$$E = C_w F_c \frac{100}{\%CO_{2w}}$$

Method 23

Equation 23-1

$$RRF_i = \frac{1}{n} \sum_{j=1}^{n} \frac{A_{cij} m^*_{ci}}{A^*_{cij} m_{ci}} -$$

Equation 23-2

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}}$$

Equation 23-3

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*}$$

Equation 23-4

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} x100\%$$

Equation 23-5

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*}$$

Equation 23-6

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} x100\%$$

Equation 23-7

$$MDL = \frac{2.5 A_{ai} m_i^*}{A_{ci}^* RRF_i}$$

Equation 23-8

$$C_{Tr} = \sum_{i=1}^{n} C_i$$

Method 25

Equation 25-1

$$\Delta P = 0.01 \frac{FP_b \theta}{V_t}$$

Equation 25-2

$$V_s = 0.3857 V \left[\frac{P_f}{T_f} - \frac{P_{fi}}{T_{fi}} \right]$$

Equation 25-3

$$C_t = \left[\frac{\frac{P_{ff}}{T_{ff}}}{\frac{P_f}{T_f} - \frac{P_{fi}}{T_{fi}}} \right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} \right]$$

Equation 25-4

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} \right]$$

Equation 25-5

$$C = C_t + C_c$$

Equation 25-6

$$m_c = 0.4993 C$$

Equation 25-7

$$Percent\ \text{recovery} = 1.604 \frac{M}{L} \frac{V_v}{P} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

Equation 25-8

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

Method 25A

Equation 25A-1

$$C_c = K C_{meas}$$

Method 26

Equation 26-1

$$\mu g \frac{Cl^-}{ml} = g\ of\ NaCl\ x\ 10^3\ x\ \frac{35.453}{58.44}$$

Equation 26-2

$$\mu g \frac{Br^-}{ml} = g\ of\ NaBr\ x\ 10^3\ x\ \frac{79.904}{102.90}$$

Equation 26-3

$$\mu g \frac{F^-}{ml} = g\ of\ NaF\ x\ 10^3\ x\ \frac{18.998}{41.99}$$

Equation 26-4

$$m_{H,X} = K V_s (S_X{}^- - B_X{}^-)$$

Equation 26-5

$$m_{X2} = V_s (S_X{}^- - B_X{}^-)$$

Equation 26-6

$$C = K \frac{m_{H,X,X2}}{V_{m(std)}}$$

Method 26A

Equation 26A-1

$$\mu g \frac{Cl^-}{ml} = g\ of\ NaCl\ x\ 10^3\ x \frac{35.453}{58.44}$$

Equation 26A-2

$$\mu g \frac{Br^-}{ml} = g\ of\ NaBr\ x\ 10^3\ x \frac{79.904}{102.90}$$

Equation 26A-3

$$\mu g \frac{F^-}{ml} = g\ of\ NaF\ x\ 10^3\ x \frac{18.998}{41.99}$$

Equation 26A-4

$$m_{HX} = K V_s (S_{X-} - B_{X-})$$

Equation 26A-5

$$m_{X2} = V_s (S_{X-} - B_{X-})$$

Equation 26A-6

$$C = K \frac{m_{HX,X2}}{V_{m(std)}}$$

Method 29

Equation 29-1

$$M_{fh} = C_{a1} F_d V_{so\ln,1}$$

Equation 29-2

$$M_{bh} = C_{a2} F_a V_a -$$

Equation 29-3

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb})$$

Equation 29-4

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} \left(V_{so\ln,1}\right)$$

Equation 29-5

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} \left(V_{so\ln,2}\right)$$

Equation 29-6

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \left(V_{so\ln,3(A,B,C)}\right)$$

Equation 29-7

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C}$$

Equation 29-8

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb})$$

Equation 29-9

$$C_s = \frac{K_4 M_t}{V_{m(std)}}$$

Method 0010

$$\frac{Max\ POHC_i\ Mass}{DV_{eff(std)}} = Max\ POHC_i\ conc$$

$$\frac{LDL_{POHC}\ x\ 10}{POHC_{i\ conc}} = V_{TBC}$$

$$C_{POHC}\,(\mu g/ml)\ x\ sample\ volume(ml) = amount(\mu g)of\ POHC\ in\ sample$$

$$m_{Cl2} = S\ x\ V_2$$

$$C = K\ x\ \frac{m}{V_{m(std)}}$$

Method 0060

$$M_{fh} = C_{a1}\ F_d\ V_{soln,1}$$

$$M_{bh} = C_{a2}\ F_a\ V_a$$

Method 0030

$$C_g = \frac{Wt.\ of\ Analytes\ in\ Sample, \mu g\left(i.e. VOST\ tubes\ \&\ condensate\right)}{Volume\ of\ sample\ at\ standard\ conditions}$$

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb})$$

Method 0050

Equation 0050-4

$$m_{HCl} = S\ x\ V_s\ x\ \frac{36.46}{35.45}$$

Equation 0050-5

$$m_{Cl2} = S\ x\ V_2$$

Equation 0050-6

$$C = K\ x\ \frac{m}{V_{m(std)}}$$

Method 0051

$$m_{HCl} = S\ x\ V_s\ x\ \frac{36.46}{35.45}$$

Method 0061

$$m = (S - B)\ x\ V_{ls}\ x\ d$$

Appendix B

Abbreviations and Terminology

%CO	Percent CO by volume, dry basis
%CO2	Percent CO2 by volume, dry basis
%N2	Percent N2 by volume, dry basis
%O2	Percent O2 by volume, dry basis
0.280	Molecular weight of N2 or CO, divided by 100
0.320	Molecular weight of O2 divided by 100
0.440	Molecular weight of CO2 divided by 100
100	Conversion to percent.
13.6	Specific gravity of mercury.
18.0	Molecular weight of water, g/g mole (lb/lb mole).
3600	Conversion Factor, sec/hr.
60	Sec/min.
A	Cross sectional area of stack, m2 (ft2).
A	Absorbance of sample.
A	Analytical detection limit, µg/ml.
A1	Absorbance of the 100µg NO2 standard.
A2	Absorbance of the 200µg NO2 standard.
A3	Absorbance of the 300µg NO2 standard.
A4	Absorbance of the 400µg NO2 standard.
An	Cross-sectional area of nozzle, m2 (ft2).
B	Liquid volume of digested sample prior to aliquotting for analysis, ml.
Bws	Water vapor in the gas stream [from Method 4 (reference method) or Method 5], proportion by volume.
C	Corrected to standard conditions, mg/dsm3(lb/dscf).
C	TGNMO concentration of the effluent, ppm C equivalent.
Ca	Acetone blank residue concentration, mg/mg.

Ca	Actual concentration of SO2 in audit sample, mg/dscm.
Ca	Actual audit sample concentration, mg/dscm.
Ca1	Concentration of metal in Analytical Fraction 1A as read from the standard curve, µg/ml.
Ca2	Concentration of metal in Analytical Fraction 2A as read from the standard curve, (µg/ml).
Cc	Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
Ccm	Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO2.
Cd	Determined concentration of SO2 in audit sample, mg/dscm.
Cd	Determined audit sample concentration, mg/dscm.
CH2S	Concentration of H2S at standard conditions,mg/dscm.
Cp	Pitot tube coefficient, dimensionless.
Cp(s)	Type S pitot tube coefficient, dimensionless.
Cp(std)	Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tube is designed according to the criteria of Sections 6.7.1 to 6.7.5 of this method.
cs	Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (gr/dscf).
Cs	Concentration of a metal in the stack gas, mg/dscm.
CSO_2	Concentration of SO2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).
Ct	Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
Ctm	Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
D	Diameter of stack, in.
De	Equivalent diameter.
F	Dilution factor. Required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
F	Sampling flow rate, cc/min.
Fa	Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see Section 8.3.4.)

Fd	Dilution factor (Fd = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading Ca1. For example, if a 2 mL aliquot of Analytical Fraction 1A is diluted to 10 mL to place it in the calibration range, Fd = 5).
ΔH	Average pressure differential across the orifice meter, mm H20 (in. H20).
Hgbh	Total mass of Hg collected in the back
Hgbh2	Total mass of Hg collected in Sample Fraction 2, µg.
Hgbh3(A,B,C)	Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.
Hgbhb	Blank correction value for mass of Hg detected in back
Hgfh	Total mass of Hg collected in the front
Hgfhb	Blank correction value for mass of Hg detected in front
Hgt	Total mass of Hg collected in the sampling train, µg.
I	Percent of isokinetic sampling.
K	0.127 mm H20 (metric units); 0.005 in. H20 (English units).
K4	103 mg/µg.
Kc	Spectrophotometer calibration factor.
Kp	Velocity equation constant.
L	Length.
L	Volume of liquid injected, µl.
L1	Individual leakage rate observed during the leak-check conducted prior to the first component change, m3/min (ft3/min)
La	pretest leak-check or for a leak-check following a component change; equal to 0.00057 m3/min (0.020 cfm) or 4 percent of the average sampling rate, whichever is less.
LI	Individual leakage rate observed during the leak-check conducted prior to the "ith" component change (i = 1, 2, 3...n), m3/min cfm).
Lp	Leakage rate observed during the post-test leak-check, m3/min (cfm).
m	Mass of NOx as NO2 in gas sample, µg.
M	Molecular weight of the liquid injected, g/g mole.
ma	Mass of residue of acetone after evaporation,mg.

Mbh	Total mass of each metal (except Hg) collected in the back
Mbhb	Blank correction value for mass of metal detected in back
Mc	TGNMO mass concentration of the effluent, mg C/dsm3.
Md	Dry molecular weight, g/g mole (lb/lb mole)
Md	Molecular weight of stack gas, dry basis (see Section 8.6), g/g mole (lb/lb mole).
Mfh	Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.
Mfhb	Blank correction value for mass of metal detected in front
mn	Total amount of particulate matter collected, mg.
Ms	Molec Molecular weight of stack gas, wet basis, g/g mole (lb/lb mole).
Mt	Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.
Mw	Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
N	Total number of traverse points.
n	total number of traverse points.
N	Normality of barium standard titrant, meq/ml.
N	Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
NA	Normality of standard C6H5AsO solution, g eq/liter.
NI	Normality of standard I2 solution, g eq/liter.
NS	Normality of standard (0.1 N) Na2S2O3 solution, g eq/liter.
NT	Normality of standard (0.01 N) Na2S2O3 solution, assumed to be 0.1 NS, g eq/liter.
p	Velocity head of stack gas, mm H20 (in. H20).
P	Allowable pressure change, cm Hg.
Pb	Barometric pressure, cm Hg.
Pbar	Barometric pressure at measurement site, mm Hg (in. Hg).
Pf	Final pressure of the intermediate collection vessel, mm Hg absolute.
Pg	Stack static pressure, mm Hg (in. Hg).

pi	Individual velocity head reading at traverse point "i", mm (in.) H20.
Pi	pitch angle at traverse point i, degree.
Pl	Initial absolute pressure of flask, mm Hg (in. Hg).
Ps	Absolute stack pressure (Pbar + Pg), mm Hg (in. Hg),
Δps	Velocity head measured by the Type S pitot tube, cm (in.) H20.
Pstd	Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Δpstd	Velocity head measured by the standard pitot tube, cm (in.) H20.
Pt	Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
Ptf	Final gas sample tank pressure after pressurizing, mm Hg absolute.
Pti	Gas sample tank pressure before sampling, mm Hg absolute.
q	Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 ... q).
Qbh2	Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis . NOTE: For example, if a 10 mL aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 mL aliquot for Qbh2.
Qbh3(A,B,C)	Quantity of Hg, µg, TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis (see NOTES in Sections 12.7.1 and 12.7.2 describing the quantity "Q" and calculate similarly).
Qfh	Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis . NOTE: For example, if a 10 mL aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 11.1.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 mL aliquot for Qfh.
Qsd	Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).
R	[(mm Hg)(m3)]/[(K)(g-mole)] {21.85 [(in. Hg)(ft3)]/[(R)(lb-mole)]}.
r	Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 ... r).
Ravg	average resultant angle, degree.
RE	Relative error for QA audit samples, percent.

Ri	resultant angle at traverse point i, degree.
Sd	standard deviation, degree.
T	Sensitivity factor for differential pressure gauges.
Tf	Final absolute temperature of flask, K (R).
Tf	Final temperature of intermediate collection vessel, K.
Ti	Initial absolute temperature of flask, K (R).
Tm	Absolute DGM temperature
Ts	Stack temperature, C (F).
Ts(abs)	Absolute stack temperature, K (R).=273 + Ts for metric units, =460 + Ts for English units.
Tstd	Standard absolute temperature, 293 K (528 R).
Tt	Sample tank temperature at completion of sampling, K.
Ttf	Sample tank temperature after pressurizing, K.
Tti	Sample tank temperature before sampling, K.
V	Sample tank volume, m3.
Va	Volume of acetone blank, ml.
Va	Volume of sample aliquot titrated, ml.
Va	Volume of absorbing solution, 25 mL.
VA	Volume of C6H5AsO solution used for standardization, ml.
Va	Total volume of digested sample solution (Analytical Fraction 2A), mL
VAI	Volume of standard C6H5AsO solution used for titration analysis, mL.
Vaw	Volume of acetone used in wash, ml.
Vf	Volume of flask and valve, ml.
Vf1B	Volume of aliquot of Analytical Fraction 1B analyzed, ml. NOTE: For example, if a 1 mL aliquot of Analytical Fraction 1B was diluted to 50 mL with 0.15 percent HNO3 as described in Section 11.1.3 to bring it into the proper analytical range, and then 1 mL of that 50
Vf2B	Volume of Analytical Fraction 2B analyzed, ml. NOTE: For example, if 1 mL of Analytical Fraction 2B was diluted to 10 mL with 0.15 percent HNO3 as described in Section 11.1.3 to bring it into the proper analytical range, and then 5 mL of that 10 mL was analyzed, Vf2B would be 0.5 ml.

Vf3(A,B,C)	Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, mL (see previous notes in Sections 12.7.1 and 12.7.2, describing the quantity "V" and calculate similarly).
VI	Volume of standard I2 solution used for standardization, ml.
VIT	Volume of standard I2 solution used for titration analysis, normally 50 ml.
Vlc	Total volume of liquid collected in impingers and silica gel (see Figure 5-6), ml.
Vm	Volume of gas sample as measured by dry gas meter, dcm (dcf).
Vm	Dry gas volume as measured by the DGM, dcm (dcf).
Vm	Volume of gas sample at meter conditions, liters.
Vm(std)	Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm(dscf).
vs	Stack gas velocity, calculated by Method 2,
vs	Average stack gas velocity, m/sec (ft/sec).
Vs	Gas volume sampled, dsm3.
Vsc	Sample volume(dry basis), ml. at standard conditions
VSI	Volume of 0.1 N Na2S2O3 solution used for standardization, ml.
Vsoln	Total volume of solution in which the SO2 sample is contained, 100 ml.
Vsoln,1	Total volume of digested sample solution (Analytical Fraction 1), ml.
Vsoln,2	Total volume of Sample Fraction 2, ml.
Vsoln,3(A,B,C)	Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.
Vt	Volume of barium standard titrant used for the sample (average of replicate titration), ml.
VT	Volume of standard (0.01 N) Na2S2O3 solution used in standardizing iodine solution (see Section 10.2.1), ml.
Vt	Sample train volume, cc.
Vtb	Volume of barium standard titrant used for the blank, ml.
VTT	Volume of standard (0.01 N) Na2S2O3 solution used for titration analysis, ml.
Vv	Intermediate collection vessel volume, m3.

Vw(std)	Volume of gas,corrected to standard conditions, scm (scf).
W	width.
W	Weight of K2Cr2O7 used to standardize Na2s2O3 or C6H5AsO solutions, as applicable (see Sections 10.2.2 and 10.2.3), g.
Wa	Weight of residue in acetone wash, mg.
xi	Individual measurements.
Y	Dry gas meter calibration factor.
Yi	yaw angle at traverse point i, degree.

Appendix C

Internet References

William T. "Jerry" Winberry, Jr.

EnviroTech Solutions

1502 Laughridge Drive

Cary, North Carolina 27511

Email: jwinberry@mindspring.com

A. Handbooks

1. *Handbook: Continuous Emission Monitoring Systems for Non-Criteria Pollutants,* U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, 20460, EPA-625/R-97-001, August 1997. Copies can be obtained from Mr. Dan Bivins, US Environmental Protection Agency, MD-19, Research Triangle Park, NC 27711, USA, 919-541-5244.

This Handbook provides a description of the methods used to continuously monitor non-criteria pollutants emitted from stationary sources. The Handbook contains a review of current regulatory programs, the state-of-the-art sampling system design, analytical techniques, and the use of computer systems for data acquisition and predictive monitoring. Such monitoring system as XRF, laser spark spectrometry, ICP, dilution systems, beta ray attenuation, out-of-stack dilution systems, etc. are covered for quantifying such non-criteria pollutants a metals, HF, HCl, organics, sulfuric and nitric acid.

2. *Engineering Manual: Quality Control Procedures For Ambient Air Monitoring at HTRW Sites,* Department of the Army, U.S. Army Engineer Division, Missouri River, Corps of Engineers, 12565 West Center Road, Omaha, Nebraska 68144-3869. Copies can be obtained from Mr. Jim Cheney, Corps of Engineers, 12565 West Center Road (CENWO-HX-C), Omaha Nebraska, USA 68144-3869, 402-697-2565.

The purpose of this Engineering Manual (EM) is to provide technical guidance in defining ambient air measurement technology and associated quality control (QC) procedures for sampling and analysis of hazardous air pollutants (HAPs) from hazardous waste or Superfund sites or in the ambient air. The EM provides direction for identifying regulatory and other remediation-specific requirements which may be generators of

ambient air monitoring needs, and provides technical guidance for defining project specific quality control requirements to support the project specific Data Quality Objectives (DQOs) for required air monitoring data.

3. *Design, Installation, and Utilization of Fixed-Fenceline Sample Collection and Monitoring Systems (FFMS),* Department of the Army, U.S. Army Engineer Division, Missouri River, Corps of Engineers, 12565 West Center Road, Omaha, Nebraska 68144-3869. Copies can be obtained from Mr. Jim Cheney, Corps of Engineers, 12565 West Center Road (CENWO-HX-C), Omaha Nebraska, USA 68144-3869, 402-697-2565.

This Engineering Manual (EM) provides details for the development and implementation of a real-time, fixed-fenceline monitoring system (FFMS) for the collection and measurement of both background and fenceline migration of onsite generated volatile organic air contaminants. The EM addresses the sample collection design requirements based on site environment, site specific contaminants, and the data quality objectives (DQOs) established for the monitoring. Management and technical personnel can use this EM to provide scope and contract language as well as oversight direction for the actual installation and operation of such fenceline monitoring systems. This EM addresses requirements for a perimeter air monitoring program during site investigation, feasibility studies, and remedial actions. The EM, complete with graphics and data tables, can be accessed via the Internet at http://www.hnd.usace.army.mil/techinfo, then click on Engineering Manual EM 200-1-5.

4. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846, Third Edition, Update III,* U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC, December 1996.

SW-846 Methods are test procedures recommended by EPA for evaluating solid waste and complying with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, as amended. The methods manual contains procedures for field and laboratory quality control, sampling, determining hazardous characteristics of wastes, and determining physical properties of wastes and guidance on how to select appropriate methods. SW-846 is now available on CD-ROM. The CD-ROM version contains valuable data tables, diagrams, chromatograms, flowcharts, and other related graphs and images along with the entire SW-846 manual. The CD-ROM allows for search by chemical name, CAS number, method number, or keyword. You can order the CD-ROM online at: http://www.ntis.gov/envlab. For the latest breaking news on SW-846, check these sites on the World Wide Web:

- EPA's Office of Solid Waste methods Team Home Page at: http://www.epa.gov/sw-846.
- NTIS Environmental Laboratory Home Page at: http://www.ntis.gov/envlab.

If you have questions concerning target analytes, method selection, method detection limits, method interferences or other concerns with using SW-846 methods, EPA has a Method Information Communication Exchange (MICE) service at http://www.epa.gov/sw-846/mice.htm.

The Methods Information Communication Exchange (MICE) Service provides a valuable and immediate means of public outreach and education. The service provides timely answers to method-related questions and takes comments on technical issues regarding the EPA Office of Solid Waste methods manual known as *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* (SW-846). The MICE Service also acts as an effective means to directly educate the public regarding inherent SW-846 method flexibility and to clarify whether a method is required by a RCRA regulation. It also documents existing issues or misconceptions regarding SW-846 methods, and thus serves as a first step in resolution of some problems. MICE was created by the OSW Methods Team and is

operated by the Team's contractor, Science Applications International Corporation (SAIC). Chemists, sampling experts, and environmentalists that are knowledgeable in SW-846 procedures are directly available through the service to those involved in RCRA-related monitoring. Persons interested in contacting the MICE Service by telephone may call a voice-mail answering service (703-821-4690) that is available 24-hours a day, 7-days a week. The caller can listen to several recorded messages on common SW-846 topics and leave a message containing a question or comment. Some of the common topics include:

- Where to order copies of SW-846;
- The status of SW-846 Updates I, II, IIA, IIB, III, and IVA;
- Where to find information on sample holding times, preservation, and storage in SW-846;
- The availability of SW-846 methods under development and other EPA methods;
- Information on RCRA characteristics testing; and.
- Solid waste sampling.

B. EPA's Compendium of Methods

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air-Second Edition,* U.S. Environmental Protection Agency, Research and Development, Center for Environmental Research Information, Cincinnati, OH, USA, EPA 625/R-96/010b.

The *Organic Compendium-Second Edition*, has been prepared to provide regional, state and local environmental regulatory agencies with step-by-step sampling and analysis procedures for the determination of selected toxic organic pollutants in ambient air. It is designed to assist those persons responsible for sampling and analysis of hazardous air pollutants (HAPs) in complying with the requirements of Title III of the Clean Air Act Amendments of 1990. The *Organic Compendium-Second Edition* contains 17 standardized sampling and analysis procedures for organic compounds, including volatile organic compounds (VOCs), pesticides, PCBs, dioxin/furans, anilines, phenols, aldehydes/ketones, polycyclic aromatic hydrocarbons (PAHs), and non-methane organic compounds. Such sampling procedures are documented including solid adsorbent methodology, whole-air specially-treated canister sampling, open path monitoring, and impinger sampling. The *Organic Compendium-Second Edition*, complete with graphics and data tables, can be accessed via the Internet at http://www.epa.gov/ttn, then click on Ambient Monitoring Technology Information Center and go to TO Methods.

2. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, U.S. Environmental Protection Agency, Research and Development, Center for Environmental Research Information, Cincinnati, OH, USA, EPA 625/R-96/010a.

The *Inorganic Compendium,* has been prepared to provide regional, state and local environmental regulatory agencies with step-by-step sampling and analysis procedures for the determination of selected toxic organic pollutants in ambient air. It is designed to assist those persons responsible for sampling and analysis of hazardous air pollutants (HAPs) in complying with the requirements of Title III of the Clean Air Act Amendments of 1990. The *Inorganic Compendium* contains 5 standardized sampling and analysis procedures for inorganic compounds, including total suspended particulate (TSP) matter, particulate matter (PM) –10, various metals, atmospheric gaseous and particulate mercury, hydrochloric acid, sulfuric acid, nitric acid, acidity of PM, and hydrogen fluoride. Such sampling procedures are documented including high volume sampling, PM-

10 sampling, annular denuder sampling and solid adsorbent sampling for gaseous mercury in the atmosphere. Analytical techniques for metals include ICP, ICP/MS, NAA, XRF, AA, and GFAA. The *Inorganic Compendium*, complete with graphics and data tables, can be accessed via the Internet at http://www.epa.gov/ttn, then click on Ambient Montirong Technology Information Center and go to IO Methods.

C. EPA Reports

1. *National Air Quality and Emissions Trends Report, 1997,* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 27711, USA, EPA-454/R-98-016.

The purpose of EPA's *Trends* document is to provide National and regional air quality trends for the criteria pollutants (CO, Pb, NO_2, O_3, PM, SO_2) regulated under the National Ambient Air Quality Standards (NAAQS). The *Trends* document discusses those areas within the US which are in nonattainment status, along with metropolitan area trends. In addition, the *Trends* document provides information associated with visibility trends and acid deposition in the US. Excellent tables, graphs, and diagrams are used to translate data into physical representation. The report, complete with graphics and data tables, can be accessed via the Internet at http://www.epa.gov/oar/aqtrnd97/.

2. *1998 Nonmethane Organic Compound (NMOC) and Speciated Nonmethane Organic Compound (SNMOC) Monitoring Program.* U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, USA, EPA-454/R-99-053, September 1999.

The *1998 Nonmethane Organic Compound (NMOC) and Speciated Nonmethane Organic Compound (SNMOC) Monitoring Program* document is a compilation of graphs and tables outlining the technical assistance provided by the U. S. Environmental Protection Agency (EPA) to various state and local agencies in the monitoring of NMOC and SNMOCs. In certain areas of the country where the National Ambient Air Quality Standard (NAAQS) for ozone is being exceeded, regulatory agencies are required to perform additional monitoring of NMOC/SNMOC. This document provides a summary of the monitoring and analytical methods employed to monitor NMOCs/SNMOCs, quality assurance and quality control activities for each of those activities, statistical evaluation of the collected data, trend charts, and summary tables for all monitoring stations throughout the US. This document can be accessed via the Internet at http://www.epa.gov/ttn/amtic, then click on Documents and Articles, then Technical Guidance.

3. *1997 Urban Air Toxics Monitoring Program (UATMP),* U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, USA, EPA-454/R-99-036, January 1999.

Similar to the Nonmethane Organic Compound (NMOC) and Speciated Nonmethane Organic Compound (SNMOC) program, the *1997 Urban Air Toxics Monitoring Program (UATMP)* document provides a summary of the monitoring and analytical methods employed to monitor speciated organics at selected sites within the United States. The document provides information on specific

site identification, speciated organic concentrations, quality assurance and quality control data associated with both sampling and analysis, statistical evaluation of the collected data, trend charts, and summary tables for all monitoring stations throughout the US. This document can be accessed via the Internet at http://www.epa.gov/ttn/amtic, then click on Documents and Articles, then Technical Guidance.

D. Environmental Databases And Web Sites

1. EPA Environmental Data and Databases

A wide variety of environmental data and databases can be downloaded or accessed through the EPA or EPA-supported web sites. Descriptions of systems managed by EPA can be found at http://www.epa.gov/epahome/Data.html. For example, the Envirofacts Warehouse (http://www.epa.gov/enviro/index_java.html) allows you to retrieve environmental information from EPA databases on Superfund sites, drinking water, toxic and air releases, hazardous waste, water discharge permits, and grants information.

-*Environmental Software and Data Files.* The National Technical Information Service (NTIS) of the U.S. Department of Commerce published a document yearly outlining the various environmental software and data files available from NTIS (www.ntis.gov.) Within the document are listed references to air, air quality models, analytical methods, environmental and physical properties of chemical substances, hazardous waste models, hazardous waste sites and toxic releases, health effects and risk assessment, regulatory requirements and enforcement, solid waste, statistical methods, water, water quality models, and waste treatment. NIST has created 13 Product Home

Pages on their site. They are:

- Product Home Page
  - Business
  - Environment
  - Health and Safety
  - International Commerce
  - Science and Technology
- Product Home Pages by Collection
  - Army Manuals and Publications
  - Best-seller
  - Databases

- Federal Computer Products Center
- International Trade Center Bookstore
- National Audiovisual Center
- Products Available by Subscription
- Published Searches—Custom Bibliographies
- NIST Technical Reports

Some of the interesting entries include:

1. ***Environmental Fate Data Base (ENVIROFATE).*** The Environmental Fate Database is a data bank or pointers to data on physical/chemical properties and environmental fate of several thousand chemicals.

2. ***Environmental Monitoring Methods Index (EMMI).*** The Environmental Monitoring Methods Index allows the user to an extensive list of analytes and analytical method involved with soil, water, waste, and air. It provides CAS numbers, regulatory lists, and regulatory limits. The database also contains method abstracts that include sample collection, storage, preservation, preparation, extraction, and analytical information. EMMI also contains information on contacts within the various offices and organizations responsible for publishing the analytical methods and regulatory information contained in EMMI.

3. ***Compendium of Superfund Field Analytical Methods.*** The *Compendium,* containing over 150 sample collection and on-site analytical methods, is provided to encourage continuity and innovation in the use of on-site field methods throughout EPA's Superfund program.

4. ***EPA, NIOSH, OSHA and SW-846 Methods on CD-ROM.*** This method database includes the complete methods as they appear in the manuals. It is a Windows operation, allowing fast searching by method number, analyte, title, type of instrumentation, CAS number or key phrases.

-*Listservers from EPA.* Find it hard to keep up with all the latest changes in environmental affairs? EPA sponsors more than 40 listservers on a wide range of environmental topics that can help keep you informed about a host of topics through your email. Topics range from EPA Press Releases to Federal Register documents on specific environmental topics to information about programs such as Green Lights. For more information on these listservers and how to subscribe, go to http://www.epa.gov/epahome/listser.htm.

1. **The Indoor Air Quality** list-"...discusses issues and concerns regarding indoor air quality." You can join this list by going to the web site, www.onelist.com/subscribe.cgi/iaq.

2. **Bioremediation Discussion Group-** "...provide a global forum for discussion of intrinsic bioremediation and enhanced bioremediation. To join, visit http://biogroup.gzea.com, select "Membership Info" and follow the directions.

3. **Commission for the Environmental Cooperation (CEC)-** "...a listserve that stimulates debate and provides information about issues pertaining to the objectives and impact of the CEC, including environmental issues of common concern in Canada, Mexico, and the United States. To join, send email to: listserv@kustserv.arizona.edu. Type in message area: subscribe CECnet "your name."

2. Chemical and Physical Properties of Hazardous Air Pollutants

An exciting database has been discovered which includes not only chemical and physical properties of hazardous air pollutants (HAPs), but references to chemical software, place to purchase chemicals, and a place to advertise laboratory equipment. It is the "dream" world of the chemist. This web site can be found at: http://chemfinder.camsoft.com. The web site has several sections addressing each of the above mentioned areas. They are:

- **ChemFinder.com**. ChemFinder is a location on the web site where you can search the data base for a chemical you enter into the search screen. You can enter the name of the chemical, formula or other identifying characteristics. The search will pull up the chemical and provide the following: melting point, boiling point, CAS RN, structure, specific gravity, vapor density, water solubility. In addition, at the end of the listing of the physical data, there is a complete reference section that links you to IR spectra database, JICST GC/MS spectra database, listing of various organizations with health effects data and exposure limits etc.
- **ChemNews.com**. ChemNews provides articles on software and computers, databases and journals, chemicals and biological, and instruments and equipment. It is an online chemical magazine and newsletter.
- **ChemStore.com**. ChemStore is the location where one can buy equipment and supplies for your laboratory online.
- **ChemACX.com.** ChemACX is the location where one can purchase chemicals online.
- **CambridgeSoft.** CambridgeSoft is the location where various chemical software packages are available. In addition, many free packages are also available for the user.

E. Environmental Web Sites

1. *U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Technology Transfer Network (TTN), Research Triangle Park, North Carolina*

- *Urban Air Toxic Website: EPA's Air Toxic Implementation Information Table.* This is a wonderful document which provides information associated with the MACT standards and also provides information on outreach materials associated with that particular MACT. This document can be found on EPA's Unified Air Toxics Web site (*http://www.epa.gov/ttn/uatw*), then click on Rules and Implementation. *Scroll down the menu until you come to* Implementation Information, *then to* NESHAP (MACT) Implementation Tools, *then to* EPA Air Toxics Implementation Information Table.

As mentioned earlier, this table contains references to other organizations that have provided outreach material for that particular MACT. Go to the Petroleum Refineries MACT and under the EPA Outreach Materials column, you will find another entry with reference to EPA's Sector Notebook for the Petroleum Refinery Industry (*http://es.epa.gov/oeca/sector/index.html*). EPA's enforcement group in Denver, Colorado has put together about 15 sector notebooks to help inspectors with their enforcement duties when visiting the particular industry. Open one of the sector notebooks (they are quite long) and find a world of information concerning that particular source category relating to operation and field inspection.

- *Urban Air Toxic Website: National Emission Standards for Hazardous Air Pollutants (NESHAP) [Also known as Maximum Achievable Control Technology (MACT)].* This site provides information on the MACT standards, including the 2, 4, 7, and 10 year bins. The table provides identification of the MACT standard in the particular bin, reference to the location of the MACT in the Code of Federal Regulations, proposed Federal Register publication and citation, and final Federal Register citation and publication. In addition, information is provided associated with technology transfer documents, including source specific category inspector "checklist." This document can be found on EPA's Unified Air Toxics Web site (http://www.epa.gov/ttn/uatw), then click on Rules and Implementation. *Scroll down the menu until you come to* Rule Information, *then to* National Emission Standards for hazardous Air Pollutants (NESHAP)[Also known as Maximum Achievable Control Technology (MACT)]. You can then click on the different tables for the various bins. It is within this section that you find reference to technology transfer involving inspector "checklist."

2. *Environmental News Network*. The *Environmental News Network* is a daily "newspaper" which you receive by your email that discusses environmental news worldwide. Links are provided to discuss environmental issues "on-line." This free subscription can be obtained by contacting newsserver2@enn.com.

F. Unique Portable Instrumentation

1. *Niton Corporation, P.O. Box 368, 74 Loomis Street, Bedford, MA 01730, 1-800-875-1578.*

The Niton Corporation has designed a new portable x-ray monitor for field screening of metals in soil and on high volume filters in the field with no laboratory analysis. The principle of operation is x-ray fluorescence with the simultaneous measurement of 15 elements. Automatic correction for cross-element interference, substrate bias and age of source is made. It is also used for rapid, on-site testing of worker exposure to metals in the workplace by evaluating 37-mm filters with the Model 700/720 Series Multi-element Metals (analyze up to 25 elements) Analyzer. Great application to screening high-volume filters for metals before shipping back to the laboratory for analysis as a "screening" tool. Visit their web site at: http://www.niton.com.

2. *Electronic Sensor Technology, 1077 Business Center Circle, Newbury Park, CA 91320, 805-480-1994.*

The Electronic Sensor Technology company has a new fast portable GC analyzer on the market that can analyze BETX in less than 30 seconds! The Model 7100 is based upon the Surface Acoustic Wave (SAW) detector resulting in identification of gaseous vapors as low as part per trillion

concentrations and amounts less than 50 picograms using the GC/SAW technique. The system is only 14" X 8" X 14 ". It has been used as a field screening tool in ambient and Superfund air monitoring studies for detecting PCBs, dioxin/furans, nerve gas (Sarin GB, Lewisite, GD, GF, VX etc.), and volatile organics. Electronic Sensor Technology can be reached and the analyzer/with chromatograms can be viewed on their web site at: http://www.estcal.com.

3. *EcoChem Analytics, 22605 Valerio Street, West Hills, CA 91307, 818-347-4369.*

EcoChem Analytics has developed a field portable real-time monitor for particle-bound polycyclic aromatic hydrocarbons (PAH) in ambient air. The Photoelectric Aerosol Sensor (PAS) works on the principle of photoionization of particle-bound PAHs using an Excimer lamp. The excited PAHs form positively charged particles which are collected on a filter within the unit. The charge of the particles is directly related to concentration of the PAHs in the gas stream. The system is 5" X 9" X 12" and weighs only 20 lbs. It can be powered off of AC or battery operated. To view this system, visit their web site at: http://www.ecochem-analytics.com.

4. *University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, North Carolina, 27516, 919-942-2753.*

University Research Glassware (URG) has developed a field portable system for collection of acidic and basic gases, fine and coarse particles, organics, and inorganics compound in the ambient air. The Versatile Air Pollutant Sampler (VAPS) has been extensively used in monitoring ambient air contaminants around Superfund sites, urban air monitoring programs, hazardous waste sites, forest fires, and oil field fires. The system has a PM10 inlet to remove particles larger than 10 um in diameter. The gas stream then passes through the Virtual Impactor (VI) where further separation of the particles occurs. The VI used in the VAPS is a modification of EPA's PM10 compliance monitor. The acid and basic gases, fine and coarse particles, organics and inorganics then are distributed to three sampling arms for collecting organic vapors on PUF foam, metals and fine particles on Teflon filter, and acidic/basic gases and acid particles using an annular denuder system. To acquire additional information, contact URG at their email address: URGCorp@compuserve.com. Their web site is under construction.

5. *Airmetrics, 2121 Franklin Boulevard, # 9, Eugene, OR 97403, 541-683-5420.*

The MiniVol Portable Air Sampler from Airmetrics offers a versatile, cost effective solution for monitoring ambient air particulates and gaseous pollutants. Compact, lightweight, battery-operated, and constructed from durable PVC, the MiniVol is ideal for field screening applications of PM10 particulate matter and sampling for ambient gases in remote locations or areas where no permanent site has been established. It has been used extensively by the EPA as a screening tool for locating Federal Reference Methods PM10 monitors in urban and ambient air sampling programs. To view this instrument, visit their web site at: http://www.airmetrics.com.

6. *Monitoring Instruments for the Environment (MIE), Inc., 7 Oak Park, Bedford, MA 01730, 617-275-1919.*

With the DataRAM, you will never again have to wait for laboratory results to assess whether airborne pollutants have reached dangerous levels. The DataRAM Real-time Portable Aerosol Monitor measures mass concentrations of airborne dust, smoke, mists, haze, and fumes and provides continuous real-time readouts. The inlet can be such that all particles are measured or a size-select inlet can be applied to determine a particular size fraction. The system can be operated off of AC or a battery. This is an excellent monitor for screening mass concentrations of particles prior to locating more traditional sampling systems. To view this instrument, visit their web site at: http://www.mieinc.com.

STACK TESTING FOR HAZARDOUS AIR POLLUTANTS (HAPs)

FIELD OBSERVATION CHECKLIST

PRETEST CHECKLIST

PRETEST MEETING CHECKLIST

Plant Name _____ Date _____
Plant Address _____

Source to be Tested _____
Plant Representative _____ Phone _____
Plant Manager _____ Phone _____
Test Team Company Name/Address _____

Team Representative _____ Phone _____
Regulatory Agency(s)/Address _____

Agency _____
Representative _____ Phone _____

Meeting Participants	Affiliation	Phone	e-mail

I. FACILITY OPERATION

A. Process

a. Process Description _____

_____

b. Method of process weight rate or fuel feed determination _____

_____

c. Process parameters (list below or use operation data sheet for process)

Process Parameters to be Monitored	Design/Normal Values	Acceptable Limits

See operations data sheet for _____

d. Acceptable values of raw material and/or fuel composition _____

e. Normal operating cycle and its effect on test plan _____

f. Test Operating Cycle _____

B. Control Devices

a. Control Device(s) _____

b. Operating Parameters (list below or use operating data sheet for process)

Operating Parameters to be Monitored	Design/normal Values	Acceptable Limits

c. Normal Operating Cycle and Periodic Maintenance (e.g., ash hopper emptying)

_____

d. Test Operating Cycle _____

C. Incinerator Information

a. Type of Incinerator: Liquid Injection_____Fixed Hearth _____
Multiple Hearth_____Rotary Kiln_____Fluidized Bed _____
Rotary Combustor _____

b. Maximum Rated Heat Input _____Btu/hr

c. Maximum Rated Air Flow _____acfm

d. Dimensions of Combustion Chamber(s) _____

_____

(Indicate Primary or Secondary)

e. Does Incinerator Include a Heat Recovery Device?_____ Yes_____ No

f. Maximum Stream Production or Hot Water Rate_____ lb/min or gal/min

g. Air Pollution Control Devices: Quench Tower_____ Pre-cooler _____
Venturi Scrubber_____ Carbon Bed_____ Packed Tower _____
Cyclone_____ Hydrosonic Jet_____ Ionizing _____

h. Fluid Bed Media _____

i. Rotation Speed _____rpm

j. Liquid Injection_____Type of Atomization _____

k. Feed Material: Solid_____ Liquid _____Gas _____Other_____

l. Maximum Feed Rate: Btu/hr_____ Gal/hr_____ Lb/hr _____ton/hr_____

m. Feed Delivery: Manual_____ Conveyor _____ Screw _____Pump_____

n. Identify Feed Streams:
No. 1:_____ No. 2:_____ No. 3:_____ No. 4: _____

II. TRIAL BURN PARAMETERS

Parameter	Item	Test Run #1	Test Run #2	Test Run #3
Feed Rate				
Heat Content of Feed				
Auxiliary Fuel Rates	Gas Oil			
Feed Composition	Water, % Ash, %			
POHC (s), % or ppm				
Other Organics				
Sulfur Content, % or ppm				
Nitrogen Cont., % or ppm				
Phosphorus Cont., % or ppm				
Metals, % or ppm				
Liquid	Viscosity Specific Gravity			
Sludges	Moisture, %			
Gases	Density			

III. INCINERATOR PARAMETERS

Parameter	Item	Test Run #1	Test Run #2	Test Run #3
Temperature	Primary Combustion Chamber			
	Secondary Combustion Chamber			
	Heat Recovery Device Inlet			
	Heat Recovery Device Outlet			
	Air Pollution Control Device Inlet			
	Air Pollution Control Device Outlet			
	Stack Gases			
Draft (in. Water)	Primary Combustion Chamber			
	Secondary Combustion Chamber			
	Heat Recovery Inlet			
	Heat Recovery Outlet			
-ESP	Unit Voltage, Kv			
	Unit Current, ma			

-Baghouse	Pressure Drop, inches			
	Air Flow Rate, acfm			
-Dry Scrubber	Lime Feed Rate, gpm			
	Air Flow Rate, acfm			
Air Flow Rates	Primary, acfm			
	Secondary, acfm			
Stack Gas Monitoring				
	Oxygen, %			
	CO_2, %			
	CO, ppm			

Parameter	Item	Test Run #1	Test Run #2	Test Run #3
	NO_x, ppm			
	HC, ppm			
	Opacity, %			
	SO_2, ppm			
	Other, ppm/%			
Feed Sample Taken?	Feed No.			
	Feed No.			
	Feed No.			
Auxiliary Fuel Samples Taken?				
Scrubber pH				
Type of Alkaline Added?				
Rate of Addition, lb/hr				
Ash Removal Rate, lb/hr				
Automatic Feed Cutoffs	Low Tempertature, F			
	High CO, ppm			
	Low Oxygen, %			

IV. TESTING METHODOLOGY TO BE DISCUSSED

Sampling Location _____
Sampling Points _____
Cyclonic Flow Check _____
Pollutant Measurement Methods _____
Mandatory Calibrations Sheets to be Provided (If not provided immediately prior to starting test program, testing should be delayed until observer receives them or authorization to proceed by Task Manager)

Orifice _____ Dry Gas Meter (Y)_____ Nozzle _____ Pitot Tube_____
Delta H@_____ Thermocouples _____ Barometer_____

Fuel, Raw Material/produce Sampling _____

Emission Rate Calculation _____

Destruction Removal Efficiency Calculation _____

Minimum Sample Volume Calculation _____

Sample Recovery Area _____

Dry Molecular Weight/dilution Determination_____
Integrated Bag_____ Grab Sample_____ Orsat _____
Fyrite_____ CEM _____

Stack or Duct Condition _____

Safety Requirements _____

Test Reporting Requirements _____

Test Schedule _____

Plant Tour _____

V. SAMPLING METHODLOLGIES TO BE USED

Pollutant Parameter	Methodology	Remarks, Additional Quality Assurance, and/or Modifications

VI. GENERAL COMMENTS

Signature of Agency Representative Affiliation of Representative Date

Signature of Plant Represnetative Date

STACK TESTING FOR HAZARDOUS AIR POLLUTANTS (HAPs)

FIELD OBSERVATION CHECKLIST

FEDERAL REFERENCE METHODS 1, 2, 3, 4, AND 5

SOURCE INFORMATION

Facility_____ Location _____
Source_____ Sampling Location_____
Test Team_____ Team Leader_____
Test Date Interval:_____/_____/_____ to _____/_____/_____
Observer_____ Affiliation_____
Sketch of sample location (if different from pretest report).
(Note: Include: duct dimensions, location of distrubances and ports, X-section showing sampling points.)
Stack or duct condition:
Material of construction: Brick_____ Concrete _____ Stainless Steel _____
Carbon steel _____ Other _____
External corrosion visible? _____
Leaks? _____
Internal corrosion? _____
Cake or pile up of particulate matter in sampling port area? _____
Remove before test? _____
Visible water droplets in stack? _____
Particulate matter appears acidic? _____
Insulation Thickness Stack under negative or positive pressure? _____
All ports accessible? _____
Nipple:
ID _____ Length _____ Capped _____
Flush with inside wall _____ Corrosion evident _____
Port dimensions:
Round diameter _____
Rectangular: L_____ W _____
Equivalent diameter _____
Facility for movement of sampling train:
Monorail _____ Skateboard and rail _____
Other _____
Electricity available? _____ No. of receptors _____
Distance to receptors _____
Ground fault circuit protection? _____ Adequate? _____
Facility for getting equipment to port _____

FEDERAL REFERENCE METHOD 1

Stack diameter properly determined? _____ Method used _____

[Note: If stack is between 4"-12" then Method 1a must be employed]
Stack Diameter? _____ Measured on site? _____
Port distance from upstream disturbance (A)_____ Upstream Diameters(A) _____
Port distance from downstream disturbance (B)_____ Downstream Diameters (B) _____
Number of Sampling Points Required?_____(Draw a line vertically from the ADistance A≅ axis down to the step chart, and from ADistance B≅ axis up to the step chart. The maximum number of points marked on the chart yields the niminum number of points to be sampled.) Actual sampling points _____
Ports and points at sampling location:
Circular: No.of Ports _____ Points/port _____
Rectangular: Grid configuration
No. of Ports_____ Points/port _____
Points located centroid of area? _____
First and last traverse points from ducts:
24 in. Diameter: 1.0 inch from wall? _____ Yes_____ No _____
12-24 in. Diameter: > 0.5 inch from wall? _____ Yes_____ No _____
Method 1 calculated correctly? _____
Points properly marked on pitot tube? _____
Port length/interior stack accounted for in calculation? _____
Cyclonic flow check verified (<20 degrees) and completed? _____
Average null point angle _____
Describe velocity profile of sampling plane _____
_____
_____

Draw picture of stack with port location and upstream/downstream disturbances marked and notated _____

Remarks _____
_____
_____
_____
_____

FEDERAL REFERENCE METHOD 2

Equipment identified matches pretest calibration list?
Pitot tube: Type S _____ Standard _____
Pitot tube coefficient _____ Calibration date _____
Design to EPA specifications? _____
Properly attached to sampling probe, if applicable? _____
Pitot tube, lines, and manometer assembled correctly? _____
Differential pressure gauge has correct sensitivity? _____
Measurement gauge: Manometer _____ Magnehelic _____ Range(s) _____
Gauge proper sensitivity for delta p range being measures? _____

Magnehelic gauges calibrated against manometer? _____ Date _____
Differential pressure gauge leveled and zeroed? _____
Visual check of pitot tube heads-good condition and meet EPA design specification? _____
_____
Pitot tube pretest leak check? _____
Cyclonic flow checked prior to test series? _____
Static pressure measured during the test series? _____
Orientation of pitot tube correct during traverse? _____
Sampling port adequately sealed around pitot tube? _____
Process operating at correct conditions? _____
Stable readings taken at each traverse point? _____
Barometric pressure recorded and adjusted for elevation? _____
(Note: Barometric pressure must be adjusted minus 0.1 A per 100 ft elevation increase or visa versa for elevation decrease. Elevation at which barometric pressure is measured compared to elevation at the test platform.)

Airport: _____ Location _____ P_b at airport _____
Sampling location elevation _____ Change in ft. _____
delta in. Hg +/- _____ (0.10 in. Hg/100 ft) _____

Stack temperature measured? _____
Stack gas moisture content determined? _____
Orsat samples taken? _____ If not, explain why _____
Posttest leak check performed? _____ Leak rate results _____
Data recorded properly _____ Calculations correct? _____
Remarks _____
_____
_____
_____
_____

FEDERAL REFERENCE METHOD 3

Method used to acquire gas sample
Single point grab _____ Single point integrated _____ Multi-point integrated _____
Type of bag _____ Type of probe _____
Pump: One way squeeze bulb _____ Diaphragm _____ Other _____
Instrument used to determine concentration ? Orsat _____ Fyrite _____ CEM _____
Is a filter used to remove particulate matter? _____
Sample train leak checked? _____
Sample train purged with stack gas prior to collecting the sample? _____
Sampling port properly sealed? _____ Sampling rate constant? _____
What rate?
Orsat performed in triplicate? _____ Analysis consistent? _____
All readings averaged and reported to nearest 0.1%? _____
Orsat:

Reagents at the proper level? _____ Analyzer level? _____

Reagents fresh?_____Date charged to orsat? _____
Analyzer leak checked?_____ Analyzed within 8 hours? _____
Sample line purged?_____Complete absorption of gases? _____
Analysis repeated until following analysis criteria met?

CO_2-any three analyses differ by

A) </= 0.3 % when CO_2 >/= 4.0 %

B) </= 0.2 % when CO_2 < 4.0 %

O_2- any three analyses differ by

A) </= 0.3 % when O_2 >/= 15.0 %

B) </= 0.2 % when O_2 < 15 %

Method 3A for O_2/CO_2:

System leak checked during test day? _____
Sample conditioner/dryer used? _____
Heated sample lines used prior to sample conditioner? _____
Moisture visible in sample lines? _____
Filter used: In-stack or out-of-stack? _____
Sample system flow rates within 10 % of calibration gas flow rates? _____
All calibration gases measured below the span value of the analyzer? _____
Data recording performed by strip chart, digital, manual or other? _____
Fuel _____ F_o Range _____
Calculate F_o: F_o = (20.9 - $\%O_2$ / $\%CO_2$)= _____

Expected Fo Range:

Anthracite/Lignite	1.015-1.130	Natural Gas	1.600-1.836
Bituminous	1.083-1.230	Wood Bark	1.000-1.120
Distillate Oil	1.260-1.413	Municipal Gargage	1.043-1.177
Residual Oil	1.210-1.370	Other	_____

Remarks _____

FEDERAL REFERENCE METHOD 4

Method used to acquire moisture concentration in stack? _____
Impinger method_____Partial pressure method_____ Wet bulb/dry Bulb _____
Nomograph _____ Other? _____
Estimate of moisture: _____
Method conducted in conjunction with pollutant emission test? _____
Preliminary run: Conducted _____ Estimated _____
Impinger method:

Impingers properly placed? _____
Impinger contents: 1st_____2nd_____3rd_____4th_____5th _____

Modifications? _____
Cooling system: Crushed ice? _____ Other _____
Sampling time per point _____ Number of points _____
Probe heater on? _____ Temperature _____ Stable _____
Crushed ice in ice bath around impingers? _____
Pretest leaks check conducted? _____ Leak rate _____
Sampling rate constant _____ Isokinetic? _____
All data recorded properly? _____
Post leak check conducted? _____ Leakage rate? _____
Recovery-Impinger Contents
Method: Volumetric? _____ Gravimetric? _____
Trip balance calibrated (gravimetric)? _____
Measurement of silica gel: Balance? _____ Other _____
Color of silica gel? _____ Condition? _____
(Note: Blue-good; pink-spent (unable to absorb water)
All analytical data recorded properly? _____
All readings averaged and reported to nearest 0.1 %? _____
Moisture value consistent with historical process values and quick-check value? _____

Remarks _____
_____
_____
_____
_____

FEDERAL REFERENCE METHOD 5

Equipment identified matches pretest calibration list? _____

Appratus:

NOZZLE

Probe nozzle: Stainless steel _____ Glass _____ Other _____
Probe design: Button-hook _____ Elbow _____ Streight tube _____
Nozzle size: _____ Calculated _____ Measured three times _____
Nozzle condition: Nicks _____ Bent opening _____

PROBE/PROBE LINER

Probe material: Borosilicate _____ Quartz _____
Stainless steel _____ Inconel _____ Other _____
Heating system: _____ Temperature _____
Water cooled? _____ Length _____

PITOT TUBE

Type: Type S _____ Standard _____ Other _____

Properly attached to probe? _____
Meets EPA guidelines for attachment to probe?_____ Yes _____ No _____
Modifications _____
Pitot tube coefficient _____

FILTER HOLDER

Construction: Borosilicate_____ Quartz _____Other _____
Frit construction: Glass frit? _____ Teflon frit? _____
Filter support _____ Silicone gasket _____
Other _____ Clean? _____
Cyclone and flask used (optional): _____

FILTER HEATING SYSTEM

Description _____
Temperature _____
Gas temperature at exit of box _____

CONDENSER

Number of impingers? _____ Clean? _____
Impinger contents: 1st_____2nd_____3rd _____
4th_____5th_____6th_____7th _____
Cooling system? _____
Proper connections? _____
Modifications? _____

METER BOX ASSEMBLY

Manufacturer _____ Model No. _____ Unit No. _____
Delta H@ value _____ Date _____
Dry gas meter AY≅ value _____ Date _____
Condition of sampling equipment? _____
Meter box leveled? _____ Timer/temperature readouts operational? _____
Manometer leveled? _____
Thermocouples calibrated? _____

Operation

Filter properly numbered and recorded on field test data sheet? _____
Filter checked visually for irregularities? _____
Filter media type? _____
Sampling site selected?_____ Stack temperature _____
Stack velocity head?_____ Stack dry molecular weight calculated? _____
Nozzle size properly selected? _____
Calibration data certified available:
Pitot tubes _____ Meter box Y factor _____
Meter box delta H@ Magnehelic guage _____ Thermocouples _____
Probe nozzle _____

Note: If calibration sheets are not available, contact Task Manager for authorization to proceed. Authorization to proceed: Yes _____ No ____

Date_____Time_____Task Manager _____

Selection of sampling points and time according to methodology? _____

Number of sample points_____Sample time/point _____

Minimum sample volume required? _____

Minimum run time required? _____

Total sample time actual? _____

Sampling train assembled properly? _____

Filter properly centered? _____ Impingers properly charged? _____

Number of impingers required? _____ Which FRM? _____

Volume in each impinger: 1st_____2nd_____3rd_____4th _____

5th_____6th_____7th_____8th _____

Drying medium: Silica gel? _____ Drierite _____

Weight _____

Pitot tube lines checked for plugging or leaks? _____

Stopcock grease used: Acetone-insoluble? _____ Heat-stable? _____

Meter box leveled?_____Manometers leveled? _____

Probe heat uniform along length of probe? _____

Dry gas meter field observation check:

A. Operating Meter Box Assembly Operate metering system for 10 minutes at the H@ value. Record the volume metered, DGM temperature and barometric pressure.

Final: DGM reading_____ft^3 Temp_____ °F P_b _____ in. Hg

Initial: DGM reading_____ft^3 Temp_____ °F P_b _____ in. Hg

Net: V_m = _____ft^3 Avg. T_m = _____ °F + 460 = _____

$Y_c = 10/V_m [0.0319 (T_m = 460)/P_b]$

Y_c = 0.97 Y = 1.03 Y = _____

Criteria: 0.97 Y < Y_c < 1.03 Y; System meets?_____ Exceeds? _____

B. Utilizing EPA's Method 5 Dry Gas Meter Performance Test Device

a. Remove the performance test device from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box.

b. Turn the power to the meter box on and start the pump.

c. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading.

d. Allow the orifice and source sampling meter obox to warm up for 45 minutes with flow controls adjusted as described in step c before starting quality assurance runs.

e. Make triplicate quality assurance runs. For each run, record initial and final dry gas meter volume, dry gas meter inlet and outlet temperatures, internal orifice pressure drop (Delta H), ambient temperature, and barometric pressure. Each run duration should be greater than 15 minutes. As the needle reaches the zero (12 o'clock) position, pump and stopwatch are stopped simultaneously. The dry gas volume and time are recorded.

QA Table For Evaluating DGM Orifice Value

Item	Run 1	Run 2	Run 3
DGM, final			
DGM, initial			
DGM, net			
DGM, T inlet (°F)			
DGM, T outlet (°F)			
DGM, T avg (°F)			
Ambient Temp. (°F)			
Pb (in. Hg)			
Orifice meter, Delta H			

f. Calculate the corrected dry gas volume for each run using the following equation:

$Y_c = 10/V_m [\ 0.0319\ (T_m = 460)/P_b]^2 =$ _____

$Y_c = 0.97\ Y = 1.03\ Y =$ _____

Criteria: $0.97\ Y < Y_c < 1.03\ Y$; System meets?_____ Exceeds? _____

Nomograph/calculator check:

a. Nomograph:

If Delta H@ = 1.80, T(meter) = 100 F, % moisture = 10 %, Ps/Pm = 1.00, calculate C.

C = _____ (0.95)

If C = 0.95, T_s = 200 F, D_n = 0.375, Delta p reference = _____ (0.118)

Align Delta p = 1.0 with Delta H = 10; and lock nomograph. Set p = 0.01.
Read Delta H_____ (0.01)
Nomograph O.K.? _____

b. Calculator:

Calculate Delta H/delta p using the following equation:

$$\text{Delta H/Delta p} = \{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_d T_m P_s/M_s T_s P_m)\}$$

= _____
= _____
= _____

Parameters for calculator check:

Item	Dimensions	Given	Calculated
A. Orifice meter coefficient, Delta H@	in. Water	1.80	_____
B. Pitot tube coefficient, Cp	dimensionless	0.84	_____
C. Abs. stack pressure, $P_s = P_b + P_{st}$	in. Hg	29.96	_____
D. Abs. meter pressure, P_m +/- P_b	in. Hg	29.92	_____
E. Abs. meter temperature, $T_m = t_m + 460$	degrees R	560	_____
F. Abs. stack temperature, $T_s = t_s + 460$	degrees R	760	_____
G. Dry molecular weight, M_{wd}	lb/lb-mole	30	_____
H. Moisture content, B_{ws} + % water/100	dimensionless	0.10	_____
I. Exact nozzle diameter, D_n	in.	0.375	_____
J. Average velocity head, Delta p	in. Water	0.1	_____
K. K factor = Delta H/Delta p		13.24	(_____)
L. Delta H calculated for delta p = 0.1	in. Water	1.324	(_____)

Calculator equation set-up O.K.? _____

Nomograph /calculator setup:

A. Delta H@ = _____
B. C_p = _____
C. P_s = _____
D. P_m = _____
E. T_m = _____
F. T_s = _____
G. M_d = _____
H. % M = _____
I. C Factor = _____
J. D_n desired = _____ in. Actual _____ in.

K. Avg. Delta p = _____

L. Delta H calculated = _____

Nomograph set up O.K.? _____

Calculator set up O.K.? _____

K-facotr figured properly? _____

Care taken to avoid scrapping nipple or stack wall? _____

Effective seal made around probe when in-stack? _____

Pretest leak check performed? _____

Probe moved at proper time? _____

Pitot tube/probe marking correct for correct sampling points? _____

Nozzle and pitot tube parallel to stack wall at all times? _____

Filter changed during run? _____

Any particulate loss during changing? _____

Leak check before changing components during run? _____

Data sheets completed, in ink, and data properly recorded? _____

Percent isokinetics calculated at each point?_____Within 90-110 %? _____

Perform % isokinetic rate check:

Delta H/Delta p = $\{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_dT_mP_s/M_sT_sP_m)\}$

= K-factor changed during run?_____ New K-factor_____

Velocity pressures and orifice pressure readings recorded accurately? _____

Post-test leak check performed? (Mandatory) _____

Leakage rate_____@ in. Hg _____

If data sheets cannot be copied, record approximate stack temperature, average stack velocity delta p, average stack delta H, approximate stack gas moisture, approximate dry stack gas molecular weight nozzle diameter, pitot tube coefficient.

Gas density determination: Temp. sensor type _____ Pressure gauge _____

Temperature sensor attached to probe?_____ Other _____

Recovery:

Construction of probe recovery brushes: Nylon_____ Clean _____Other _____

Wash bottle: Clean? _____

Storage containers: Borosilicate glass?_____ Other_____ Clean?_____

Leak free? _____

Petri-dishes: Glass? _____ Polyethylene_____ Other_____ Clean? _____

Graduated cylinder/or balance: Subdivisions </= 2 mL?_____Other _____

Balance type?_____Calibrated? _____

Plastic storage containers: Air-tight?_____Clean?_____

Probe allowed to cool sufficiently? _____

(Note: Cap placed over nozzle tip to prevent loss of particlate matter?)

During sampling train disassembly, are all openings capped? _____

Clean-up area: Description _____

_____

_____

Clean-up area clean and protected from wind? _____
Filter handling: Tweezers used?_____Material of construction? _____
Surgical gloves worn?_____Other _____
Any particulate matter spilled? _____
Water: Distilled? _____
Stopcock grease: Acetone-insoluble?_____Heat-stable Silicone? _____
Probe handling: Acetone rinse?_____Distilled water rinse? _____
Particulate recovery: Probe nozzle?_____Probe fitting? _____
Probe liner?_____Front half of filter holder? _____
Blanks: Acetone_____Distilled water _____
Acetone reagent <.001 % residue? _____
Glass bottles residue <.001 %?_____
Acteone blanks residue <.001 %_____
Any visible particles on filter holder inside probe? _____
Color of silica gel?_____Condition? _____
Method of silica gel transfer? _____
All jars adequately labeled? _____
Jars sealed tightly?_____Liquid level marked on jars? _____
Jars locked up and chain-of-custody completed? _____
All data forms signed and chain-of-custody completed? _____

Remarks _____
_____
_____
_____
_____
_____

SOURCE SAMPLING FOR HAZARDOUS AIR POLLUTANTS (HAPs)

FIELD OBSERVATION CHECKLIST

SW-846, METHOD 0010

SAMPLING AND ANALYSIS
FOR
SEMI-VOLATILE ORGANIC COMPOUNDS

SOURCE INFORMATION

Facility _____
Location _____
Source _____
Sampling Location _____
Test Team _____
Team Leader _____
Test Date Interval: ____/____/____ to ____/____/____
Observer _____
Affiliation _____

PRETEST MEETING CHECKLIST

Please reference Pretest Checklist

FEDERAL REFERENCE METHODS 1 THROUGH 5

Please reference Federal Reference Methods 1 through 5 Checklist.

SW-846, METHOD 0010

SAMPLING AND ANALYSIS FOR SEMI-VOLATILE ORGANIC COMPOUNDS

Equipment identified matches pretest calibration list? _____

Apparatus:

NOZZLE

Probe nozzle: Stainless steel_____ Glass_____ Other_____
Probe design: Button-hook_____ Elbow_____ Streight tube_____
Tapered (30 angle)? _____
Nozzle size:_____ Calculated_____ Measured three times _____

Nozzle condition: Nicks_____Bent opening _____

PROBE/PROBE LINER

Probe material: Borosilicate_____Quartz_____Stainless steel _____
Inconel_____Other _____
Heating system:_____Temperature (120 C +/- 14 °C) _____
Water cooled?_____Length _____
Probe liner: Borosilicate/quartz (up to 480 °C)_____Quartz(480-900 °C)_____
Temperature sensor attached to probe?_____
Temperature sensor placed in an interference-free arrangement with probe? _____

PITOT TUBE

Type: Type S_____Standard_____Other _____
Properly attached to probe?_____
Meets EPA guidelines for attachment to probe?_____Yes_____No _____
Modifications _____
Pitot tube coefficient_____

FILTER HOLDER

Construction: Borosilicate_____Quartz_____Other _____
Frit construction: Glass frit?_____Teflon frit?_____
Filter support_____Silicone gasket_____
Other_____Clean? _____
Cyclone and flask used(optional):_____

FILTER HEATING SYSTEM

Description _____
Temperature (120+/- 14 °C _____
Gas temperature at exit of Box _____

ORGANIC SAMPLING MODULE

Three sections: Condenser_____Sorbent trap_____
Condensate knockout trap_____
Condenser maintains stack gas not exceeding 20 °C (68 °F)? _____
Sorbent trap jacketed to maintain internal gas temperature not exceeding 20°C (68°F)?_____
Design of sorbent trap: Single unit?_____Dual units? _____
Thermocouple well in bed of sorbent Trap?_____
Sorbent in trap? (XAD-2?)_____20 grams?_____
Sorbent certified clean (< 10 ng per target analyte?)? _____
Date of sorbent certification?_____Within 4 weeks?_____
Chain-of-custody with sorbent trap?_____
Sorbent trap received wrapped in aluminum foil? _____
Coolant? (Ice water?) _____
Knockout trap directly below sorbent trap? _____
Type of knockout trap? _____

Impinger stem in knockout trap one-half length of normal stem? _____

IMPINGER TRAIN

Number of impingers?_____Clean? _____
Impinger contents: 1st (Water?)_____2nd (Water?) _____
3rd (Empty/ or caustic solution?)_____4th (Silica Gel?) _____
5th_____6th_____7th_____8th _____
Volume/weight of contents of impingers: 1st (100 mL?)_____2nd (100 mL?)_____
3rd (Empty?)_____4th (200-300 g silica gel?)_____
5th_____6th_____7th_____8th _____
Impinger types: Greenburg-Smith?_____Standard?_____
Impinger tip design: Tapered tip?_____Standard tip? _____
Cooling system? _____
Proper connections? _____
Modifications? _____

METER BOX ASSEMBLY

Manufacturer_____Model No._____Unit No. _____
Delta H@ value_____ Date _____
Dry gas meter "Y" value_____ Date_____
Dry gas meter measure volume within 1 %? _____
Condition of sampling equipment?_____
Meter box leveled? _____
Timer/temperature readouts operational? _____
Manometer leveled? _____
Thermocouples calibrated (Read within 3 C?)? _____
Barometer: Mercury_____Aneroid_____Other _____
Barometer capable of measuring atmospheric pressure within 2.5 mm Hg? _____

Operation

Filter properly numbered and recorded on field test data sheet? _____
Filter type: Glass?_____Quartz-fiber? _____
Filter has organic binder (Method requires no organic binder)?_____
Filter manufacturer_____Filter manuf. Number_____
Filter weighted to constant weight/recorded? _____
Filter checked visually for irregularities? _____
Filter collection efficiency meets EPA's specification of 99.95 %?_____
Stopcock grease used is solvent-insoluble, heat-stable silicone grease? _____
Sampling site selected?_____Stack temperature _____
Stack velocity head?_____Stack dry molecular weight calculated?_____
Nozzle size properly selected? _____
(Note: During sampling run, nozzle can not be changed!)
Calibration data certified available: Pitot tubes_____Meter box Y factor _____
Meter box delta H@_____Magnehelic guage _____
Thermocouples_____Probe nozzle _____

(Note: If calibration sheets are not available, contact Task Manager for authorization to proceed. Authorization to proceed: Yes_____No_____
Date_____Time_____Task Manager _____)
Selection of sampling points and time according to methodology? _____
Number of sample points_____Sample time/point_____
Minimum sample volume required (3 dscm or 105.9 scf)? _____
Minimum run time required? _____
Total sample time actual? _____
Probe can reach all traverse points? _____
Sampling train assembled properly?_____
(Note: During preparation of sampling train, keep all openings where _____ conta
Filter properly centered?_____Impingers properly charged? _____
Number of impingers required?_____Which FRM? _____
Volume in each impinger: 1st_____2nd_____3rd_____4th_____
5th_____6th_____7th_____8th _____
Distilled organic-free water (Type II) used?_____
Drying medium: Silica gel?_____Drierite _____
Weight (200-300 grams?)_____6-16 mesh?_____
Pitot tube lines checked for plugging or leaks? _____
Stopcock grease used: Acetone-insoluble?_____Heat-stable?_____
(Note: Do not use stopcock grease upstream of sorbent bed!)
Meter box leveled?_____Manometers leveled? _____
Probe heat uniform along length of probe?_____
If glass liner used, install nozzle using Viton-A O-ring when stack temperatures are< 260°C_____Woven glass-fiber gasket >260°C_____

Dry gas meter field observation check:

A. Operating Meter Box Assembly

Operate metering system for 10 minutes at the Delta H@ value. Record the volume metered, DGM temperature and barometric pressure.

Final: DGM reading_____ft^3 Temp_____°F P_b_____ in. Hg
Initial: DGM reading_____ft^3 Temp_____°F P_b_____ in. Hg
Net: V_m = _____ft^3 Avg. T_m = _____°F + 460 = _____

$Y_c = 10/V_m [0.0319 (T_m = 460)/P_b]^2$ = _____

$Y_c = 0.97$ Y = _____
1.03 Y = _____

Criteria: 0.97 Y < Y_c < 1.03 Y; System meets?_____ Exceeds?_____

B. Utilizing EPA's Method 5 Dry Gas Meter Performance Test Device

a. Remove the performance test device from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box.
b. Turn the power to the meter box on and start the pump.
c. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading.
d. Allow the orifice and source sampling meter box to warm up for 45 minutes with flow controls adjusted as described in step c before starting quality assurance runs.
e. Make triplicate quality assurance runs. For each run, record initial and final dry gas meter volume, dry gas meter inlet and outlet temperatures, internal orifice pressure drop (Delta H), ambient temperature, and barometric pressure. Each run duration should be greater than 15 minutes. As the needle reaches the zero (12 o'clock) position, the pump and stopwatch are stopped simultaneously. The dry gas meter volume and time are recorded.

QA Table For Evaluating DGM Orifice Value

Item	Run 1	Run 2	Run 3
DGM, final			
DGM, initial			
DGM, net			
DGM, T inlet (°F)			
DGM, T outlet (°F)			
DGM, T avg (°F)			
Ambient Temp. (°F)			
Pb (in. Hg)			
Orifice meter, Delta H			

f. Calculate the corrected dry gas volume for each run using following equation:

$Y_c = 10/V_m [\ 0.0319\ (T_m = 460)/P_b]^2 =$ _____

$Y_c = 0.97\ Y =$ _____
$1.03\ Y =$ _____

Criteria: $0.97\ Y < Y_c < 1.03\ Y$; System meets?_____ Exceeds? _____

Nomograph/calculator check:

a. Nomograph:

If Delta H@ = 1.80, T(meter) = 100 F, % moisture = 10 %, Ps/Pm = 1.00, calculate C.

C = _____ (0.95)

If C = 0.95, T_s = 200 F, D_n = 0.375, Delta preference = (0.118)

Align Delta p = 1.0 with Delta H = 10; and lock nomograph. Set p = 0.01.
Read Delta H_____ (0.01)
Nomograph O.K.?_____

b. Calculator:

Calculate Delta H/delta p using the following equation:

$$\text{Delta H/Delta p} = \{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_d T_m P_s/M_s T_s P_m)\}$$

= _____
= _____
= _____

Parameters for calculator check:

Item	Dimensions	Given	Calculated
A. Orifice meter coefficient,	Delta H@ in. Water	1.80	_____
B. Pitot tube coefficient,	Cp dimensionless	0.84	_____
C. Abs. stack pressure,	$P_s = P_b + P_{st}$ in. Hg	29.96	_____
D. Abs. meter pressure,	P_m +/- P_b in. Hg	29.92	_____
E. Abs. meter temperature,	$T_m = t_m$ + 460 degrees R	560	_____
F. Abs. stack temperature,	$T_s = t_s$ + 460 degrees R	760	_____
G. Dry molecular weight,	M_{wd} lb/lb-mole	30	_____
H. Moisture content,	B_{ws} + % water/100 dimensionless	0.10	_____
I. Exact nozzle diameter,	D_n in.	0.375	_____

J. Average velocity head, Delta pin. Water 0.1 _____
K. K factor = Delta H/Delta p13.24 (_____)
L. Delta H calculated for delta p = 0.1 in. Water1.324 (_____)
Calculator equation set-up O.K.? _____

Nomograph /calculator setup:

A. Delta H@ = _____
B. C_p = _____
C. P_s = _____
D. P_m = _____
E. T_m = _____
F. T_s = _____
G. M_d = _____
H. % M = _____
I. C Factor = _____
J. D_n desired = _____ in. Actual in.
K.Avg. Delta p = _____
L. Delta H calculated = _____

Nomograph set up O.K.? _____
Calculator set up O.K.? _____
K-facotr figured properly? _____
Care taken to avoid scrapping nipple or stack wall? _____
Effective seal made around probe when in-stack? _____
Pretest leak check performed? _____
Probe moved at proper time? _____
Pitot tube/probe marking correct for correct sampling points? _____
Nozzle and pitot tube parallel to stack wall at all times? _____
Filter changed during run? _____
Any particulate loss during changing? _____
Leak check before changing components during run? _____
Data sheets completed, in ink, and data properly recorded? _____
Percent isokinetics calculated at each point? _____ Within 90-110 %? _____
Perform % isokinetic rate check:

Delta H/Delta p = $\{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_d T_m P_s / M_s T_s P_m)\}$ =

K-factor changed during run? _____ New K-factor _____
Velocity pressures and orifice pressure readings recorded accurately? _____
Post-test leak check performed? _____ (Mandatory)
Leakage rate _____ @ in. Hg _____
If data sheets cannot be copied, record approximate stack temperature, average stack velocity delta p _____, average stack delta H _____, approximate stack gas moisture _____,

approximate dry stack gas molecular weight _____, nozzle dia
Gas density determination: Temp. sensor type_____Pressure gauge _____
Temperature sensor attached to probe?_____Other _____

Recovery:

Post-test leak check performed (Mandatory)? _____
Construction of probe recovery brushes: Nylon_____Clean_____Other____
Wash bottle: Clean?_____Three?_____Teflon/Glass? _____
Storage containers: Borosilicate glass?_____Other_____Clean?_____
Leak free?_____Teflon liners? _____
Petri-dishes (For storage/transport of filters):
Glass_____Polyethylene_____Other_____Clean?_____
Graduated cylinder/or balance: Subdivisions </= 2 mL?_____Other_____
Balance type?_____Calibrated? _____
Plastic storage containers (To store silica gel): Air-tight?_____Clean?_____
Probe allowed to cool sufficiently?_____
(Note: Cap placed over nozzle tip to prevent loss of particlate matter?)
During sampling train disassembly, are all openings capped? _____
Clean-up area: Description _____
Clean-up area clean and protected from wind?_____
Filter handling: Tweezers used?_____Material of construction?_____
Surgical gloves worn?_____Other _____
Any particulate matter spilled? _____
Water: Distilled?_____
Stopcock grease: Acetone-insoluble?_____Heat-stable Silicone? _____
Probe handling: Acetone rinse?_____Distilled water rinse? _____
Particulate recovery: Probe nozzle?_____Probe fitting? _____
Probe liner?_____Front half of filter holder? _____
Blanks: Methanol_____Methylene chloride_____
Any visible particles on filter holder inside probe? _____
Color of silica gel?_____Condition? _____
Method of silica gel transfer? _____
All jars adequately labeled? _____
Jars sealed tightly?_____Liquid level marked on jars? _____
Jars locked up and chain-of-custody completed? _____
Methylene chloride/methyl alcohol used in recovery? _____
Distilled-in-glass grade? _____
Resin bed capped at both ends? _____
Knockout trap capped? _____
Liquid in impinger train (first three impingers) measured/weighted? _____

Shipping Containers:

Container #1 (Petri dish): Filter inside? _____
Container #2 (Probe assembly rinse): Rinse with methanol/methylene chloride? _____
Container #3 (Sorbent trap): Labeled/ends sealed? _____

Container #4 (Condensate trap): Labeled/volume measured? _____

Container #5 (Train component rinse): From filter to 1st impinger: _____

Labeled/volume measured? _____

Container #6 (Silica gel): Color noted/capped/weighted. Containers #2-5 stored under "blue ice " (<4 C) and during shipment? Container #1 shipped unrefrigerated?

All data forms signed and chain-of-custody completed? _____

Remarks _____

_____

_____

_____

_____

STACK TESTING FOR HAZARDOUS AIR POLLUTANTS

FIELD OBSERVATION CHECKLIST

SW-846, METHOD 0030 AND METHOD 0031

SAMPLING AND ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

SOURCE INFORMATION

Facility_____Location _____
Source_____Sampling Location_____
Test Team_____Team Leader_____
Test Date Interval:_____/_____/_____ to _____/_____/_____
Observer_____Affiliation_____

PRETEST MEETING CHECKLIST

Please reference Pretest Checklist

FEDERAL REFERENCE METHODS 1 THROUGH 5

Please reference Federal Reference Methods 1 through 5 Checklist.

SW-846, METHOD 0030

VOLATILE ORGANIC SAMPLING TRAIN (VOST)

Equipment identified matches pretest calibration list?_____
Principle organic hazardous constituents (POHCs) 1._____2. _____
3._____4._____5._____6._____
7._____8._____9._____10._____
For each waste feed stream stream containing POHCs, calculate POHC feed rate:

1. POHC concentration in waste feed:_____%
2. Waste feed rate lb/hr
   If liquid feed rateis gal/hr: _____
   gal/hr X _____lb/gal (density) = lb/hr
3. POHC feed rate in each waste feed stream:
   _____ decimal wt (% POHC) X _____waste feed rate (lb/hr) = ___ lb POHC/hr

Verification of Method 0030 (VOST) sample volume to be collected:

1. Basis:-% Destruction Removal Efficiency (DRE) expected, %
   -Quantity of POHC to be collected, ng.

-Calibration range of GC/MS, ng (0-3,000 ng)

2. Calculation: Quantity of POHC to be collected:

Quantity collected (ng), = [A X (1-B) X C X D X E]/ (F X G X H)

Where:

A = POHC feed rate, lb/hr
B = DRE (as decimal)
C = 453. 59 g/lb
D = Sample volume, L
E = 1 X 10^9 ng/g
F = 60 min/hr
G = Stack gas flow rate, dscfm
H = 28.316 L/ft^3

3. Perform calculation for:
   % DRE of 99.9; 99.99; 99.999 and 99.9999
   Sample volumes: 5, 10, 15, and 20 liters
4. Consturct matrix for % DREs and sample volumes:

	Total ng collected			
% DRE	5 L	10 L	15 L	20 L
99.9				
99.99				
99.999				
99.9999				

5. Selection of sample volume:

At the required DRE, select the total volume to be sampled so that the maximum ng collected will be within the mid-range of the calibration curve. Sample volume must not exceed 20 liters.

Sample volume: _____ Lpm

6. Sampling rate:

The sampling rate is dependent on the total sampling time and total volume to be collected and must be between 0.25 and 1.0 Lpm. At no time shall sample rate exceed 1.0 Lpm.

Sampling rate: _____ Lpm

7. Total sample time per cartridge set:

Method 0030, VOST < 20 min? _____
Method 0031, SLO-VOST < 40 min? _____

8. Total number of cartridge sets per run:

Minimum of 4 sets? _____
Maximum of 6 sets? _____

9. Run time (2 hours actual):

Method 0030, VOST < 80 min ? _____
Method 0031, SLO-VOST < 160 min? _____

Appratus:

NOZZLE

Probe nozzle: Stainless steel_____ Glass_____ Other _____
Probe design: Button-hook_____ Elbow_____ Streight tube_____
Tapered (30 angle)? _____
Nozzle size:_____ Calculated_____ Measured three times _____
Nozzle condition: Nicks_____ Bent opening _____

PROBE/PROBE LINER

Probe material: Borosilicate_____ Quartz_____ Stainless steel _____
Inconel_____ Other _____
Heating system:_____ Temperature (120 °C +/- 14 °C) _____
Water cooled?_____ Length _____
Probe liner: Borosilicate/quartz (up to 480 °C)_____ Quartz(480-900 °C)_____
Temperature sensor attached to probe?_____
Temperature sensor placed in an interference-free arrangement with probe? _____
Temperature probe calibrated?_____ Yes_____ No_____ Date_____
Probe plug used?_____ Teflon? _____

PITOT TUBE (If Applicable)

Type: Type S_____ Standard_____ Other _____
Properly attached to probe?_____
Meets EPA guidelines for attachment to probe?_____ Yes_____ No _____
Modifications _____
Pitot tube coefficient _____

SAMPLE TRANSFER LINE

Construction: Borosilicate_____ Quartz_____ Teflon_____
Length (< 5ft)?_____ Heat trace? _____
Other_____ Clean? _____

Isolation valve?_____Quantity?_____Stainless steel?_____

ORGANIC SAMPLING MODULES

Three sections: condenser_____sorbent trap _____
condensate knockout trap _____
Condenser maintains stack gas not exceeding 20 °C _____
Condenser: water cooled?_____coolant? _____
Sorbent trap jacketed to maintain the internal gas temperature not exceeding 20 °C (68 °F)? _____
Design of sorbent trap: Single unit?_____Dual units? _____
Thermocouple well in bed of sorbent trap? _____
Sorbent in traps?1._____2._____3. _____
Sorbent certified clean (< 10 ng per target analyte?)? _____
Date of sorbent certification?_____Within 4 weeks?_____
Sorbent stored < 4 °C before use?_____
Chain-of-custody with sorbent trap?_____
Sorbent trap received wrapped in aluminum foil? _____
Coolant? (Ice water?) _____
Knockout trap directly below sorbent trap? _____
Type of knockout trap? _____
Vacuum grease of any kind PROHIBITED!_____

METER BOX ASSEMBLY

Manufacturer_____Model No._____Unit No. _____
Dry gas meter measuresin liters?_____Yes_____No _____
Dry gas meter "Y" value_____Date _____
Dry gas meter measure volume within 1 %? _____
Rotameters calibrated?_____Yes _____ No
Calibration date? _____
Condition of sampling equipment?_____
Meter box leveled? _____
Timer/temperature readouts operational? _____
Manometer leveled? _____
Thermocouples calibrated (Read within 3 °C?)? _____
Barometer: Mercury, Aneroid, Other_____
Barometer capable of measuring atmospheric pressure within 2.5 mm Hg? _____
Vacuum gauge: After silica gel trap?_____Range (0-30 " Hg)? _____
Isolation valve: Located after vacuum gauge? _____
Leak free pump? _____
Temperature readouts: Digital?_____Analog?_____Dial Thermometer? _____
Barometer: Anaroid?_____Mercury? _____
Calibrated against_____Date:_____
AirportLocation_____
Elevation _____ feet above sea level
Sampling location elevation _____ feet above sea level

Station Pb _____

[Inches of Hg to be added or subtracted from Station Pb (0.1 " Hg X ft per 100 ft)

Describe condition of sampling equipment: _____

_____

_____

_____

Operation

Sampling site selected?_____Stack temperature _____

Stack velocity head?_____Stack dry molecular weight calculated?_____

Nozzle size properly selected (if applicable)? _____

Calibration data certified available: Pitot tubes_____Meter box Y factor _____

Rotameters_____Magnehelic guage_____

Thermocouples_____Probe nozzle_____

(Note: If calibration sheets are not available, contact Task Manager for authorization to proceed. Authorization to proceed: Yes_____No _____

Date_____Time_____Task Manager _____

Selection of sampling points and time according to methodology? _____

Number of sample points_____Sample time/point_____

Minimum sample volume calculated per cartridge set: _____

Minimum run time required? _____

Total sample time actual? _____

Sampling point > 1 meter from side of wall? _____

Sampling point at average stack gas velocity? _____

Average stack gas temperature? _____

Sampling train assembled properly? _____

(Note: During preparation of sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil.)

Sorbent traps properly orientated in sampling train? _____

List orientation of sorbent cartridges:1._____2._____3. _____

Drying medium: Silica gel?_____Drierite _____

Pitot tube lines checked for plugging or leaks? _____

Meter box leveled?_____Manometers leveled? _____

Probe heat uniform along length of probe?_____

Condenser water recirculating properly? _____

Care taken to avoid scrapping nipple or stack wall?_____

Effective seal made around probe when in-stack? _____

Pretest leak check performed (Required)?_____Leak rate <0.1 " Hg? _____

Leak check performed through probe? _____

Pitot tube/probe marking correct for correct sampling point? _____

Pitot tube parallel to stack wall at all times? _____

Data sheets completed, in ink, and data properly recorded?_____

Probe maintained at 120 +/- 14 °C? _____

Gas temperature exiting sorbent bed at a maximum of 20 °C?_____
Data recorded on field data sheet properly? _____

Recovery:

Storage containers: Borosilicate
glass?_____Other_____Clean? _____
Leak free?_____Teflon liners? _____

Clean-up area: Description

Clean-up area clean and protected from wind?_____
Recovery personnel cover hands with cotten gloves for sorbent tubes recovery? _____
Sorbent cartridges capped at both ends?_____
Sorbents properly marked for particular run?_____
Sorbents stored at < 4 °C until analyzed? _____
Knockout trap capped? _____
All data forms signed and chain-of-custody completed? _____
_____
_____

SW-846, METHOD 0030/0031 TEST OBSERVATION SHEET

1. GENERAL						
a. Date b. Run No. C. Code No.						
2. CARTRIDGE INFORMATION	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**
a. Cartridge ID - Cartridge No. 1 - Cartridge No. 2 - Cartridge No. 3 Certificate of Cleaniness? (Yes/No)						
3. TRAIN SET-UP						
a. Cartridges Placed Properly and Correctly Oriented? (Yes/No) b. Condensers Operating Properly? c. Condenser Trap in Place? d. Silica Gel in Place? e. Probe at Operating Temperature?						
4. TRAIN LEAK CHECK						
Initial a. Checked @ - 10 " Hg? b. Leak Rate (<0.1 " Hg for 1 min.)? c. Vented through Charcoal Tube? **Intermittent** a. Checked at Highest Vacuum? b. Leak Rate (< 0.1 " Hg for 1 min.)? c. Vented through Charcoal Tube?.						

SW-846, METHOD 0030/0031 TEST OBSERVATION SHEET (CON'T)

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
5. TRAIN OPERATION						
a. Probe in Stack At Sampling Point?						
b. Sample Port Sealed?						
c. Stack Gas Purged Through Probe via Isolation Valve Prior To Starting Run?						
d. Valve Opened for Condenser?						
e. Inlet to 1st Sorbent < 20 °C?						
f. Test Time:						
- Run Start						
- Run End						
- Net Sampling Time						
- Sampling Rate						
- Minimum Sampling Time Met?						
h. Dry Gas Meter						
- Final (L)						
- Initial (L)						
- Net (L)						
- Minimum Volume of Liters Met?						
6. SAMPLE RECOVERY						
a. Cartridges Removed With Gloved Hands and End Caps Replaced?						
b. Cartridges Properly Labeled?						
c. Cartridges Stored at < 4 °C?						
d. Condensate Recovered in Vial and Topped Off With DI Water?						
e. Condensate Vial Properly Labeled?						
f. All Samples Logged Into Master Field Log Book?						
g. Chain-of-Custody Completed and Signed?						

SW-846, METHOD 0030/0031 TEST OBSERVATION SHEET (CON'T)

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
7. BLANKS						
a. **Field Blank:** For Every 6 Cartridge Sets, Obtain One Set, Place Near Sampling Train For 5 Minutes, Replace Caps, Store < 4° C. - Field Blank Set Taken? - Labeled Properly? - Stored Properly < 4 °C?						
b. **Trip Blank:** For Every 6 Cartridge Sets, Obtain One Set, Do Not Uncap, Store < 4 °C. - Trip Blank Set Taken? - Labeled Properly? - Stored Properly < 4 °C?						
c. **Field Blank D.I. Water:** Fill One Vial With Field D.I. Water to Overflow, Cap, Store. - Field Blank D.I. Water Take? - Labeled Properly? - Stored Properly?						
8. SHIPPING						
a. Chain-of-Custody Sheets Completed? b. Samples Shipped at < 4 °C? c. Shipping Mode (UPS, Fed. Exp., Other)?						

SW-846, METHOD 0030/0031 TEST OBSERVATION SHEET (CON'T)

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
9. DATA SHEETS						
a. Observer Signed Data Sheets? b. Data Sheets Submitted to Observer?						
10. AUDIT CYLINDER RUN						
a. Audit Cylinder Acquired From EPA? b. Compound Group and Range Within Guidelines? c. Source Test Team To Conduct four (4) Runs According to Audit Procedures Supplied with Kit. Can Be Conducted Either Prior To or After Scheduled Test Runs. d. Audit Runs: - Date - Time Interval - Sampler ID - Cylinder No. - Range - Expiration Date - Cylinder Pressure (Before) (After) - Run 1. Leak Check Before Run? 2. Leak Check After Run? 3. Volume Collected 4. Cartridge Sealed? 5. Cartridge Labeled Properly? 6. Cartridge Stored < 4 °C? 7. Cartridge ID Number						

STACK TESTING FOR HAZARDOUS AIR POLLUTANTS (HAPs)

FIELD OBSERVATION CHECKLIST
SW-846, METHOD 0060

DETERMINATION OF METALS IN STACK EMISSIONS

SOURCE INFORMATION

Facility_____Location _____
Source_____Sampling _____ Location
Test Team_____Team Leader_____
Test Date Interval:_____/_____/_____ to _____/_____/_____
Observer_____Affiliation_____

PRETEST MEETING CHECKLIST

Please reference Pretest Checklist

FEDERAL REFERENCE METHODS 1 THROUGH 5

Please reference Federal Reference Methods 1 through 5 Checklist.

SW-846, METHOD 0060

DETERMINATION OF METALS IN STACK EMISSIONS

Equipment identified matches pretest calibration list?_____
Particulate matter measured concurrently with metals?_____
Metals under evaluation: Sb___As___Ba___Be___Cd___Cr___Co___Cu___Pb___Mn __
Hg___Ni___P___Se___Ag___Tl___Zn___Other___Other___Other___Other _____
Mercury emissions being measured (If mercury emissions are not being measured, then impingers 4, 5, and 6 are not necessary and may be eliminated)? _____

Apparatus:

NOZZLE

Probe nozzle: Glass (Required)_____Other _____
Probe design: Button-hook_____Other _____
Nozzle size:_____Calculated_____Measured three times _____
Nozzle condition: Nicks/Chips_____

PROBE/PROBE LINER

Probe material: Borosilicate_____Quartz_____
Heating system:_____Temperature _____
Water cooled?_____Length _____

PITOT TUBE

Type: Type S_____ Standard_____ Other _____
Properly attached to probe?_____
Meets EPA guidelines for attachment to probe?_____ Yes_____ No _____
Modifications _____
Pitot tube coefficient_____

FILTER HOLDER

Construction: Borosilicate_____ Quartz_____ Other _____
Frit construction: Glass frit?_____ Teflon frit?_____
Filter support material?_____ Silicone gasket?_____
Without organic binder?_____ Clean? _____
Cyclone and flask used (optional): _____

FILTER HEATING SYSTEM

Description _____
Temperature _____
Gas temperature at exit of box _____

CONDENSER

Number of impingers?_____ Clean?_____
Teflon impingers used?_____
Impinger contents: 1st_____ 2nd_____ 3rd _____
4th_____ 5th_____ 6th_____ 7th _____
Cooling system? _____
Proper connections (leak free/ground glass/ or other material)? _____
Modifications? _____
All glassware properly cleaned as specified in methodology (Hot tap water, then hot soapy water, 3X with tap water, 3X reagent water, soaked in 10 % nitric acid for 4 hours, 3X reagent water, rinsed with acetone, then air dry, then opening covered with paraffin until use?) _____

METER BOX ASSEMBLY

Manufacturer_____ Model No._____ Unit No. _____
Delta H@ value_____ Date _____
Dry gas meter "Y" value_____ Date _____
Condition of sampling equipment?_____
Meter box leveled? _____
Timer/temperature readouts operational? _____
Manometer leveled? _____
Thermocouples calibrated? _____

Operation

Filter properly numbered and recorded on field test data sheet? _____

(Note: If particulate emissions are not to be determined, the filter need not be desiccated or weighted.)

Filter checked visually for irregularities? _____

Filter media type? _____

Sampling site selected?_____ Stack temperature _____

Stack velocity head?_____ Stack dry molecular weight calculated? _____

Nozzle size properly selected? _____

Calibration data certified available: Pitot tubes _____ Meter box Y factor _____

Meter box delta H@_____Magnehelic gauge _____

Thermocouples_____Probe nozzle _____

(Note: If calibration sheets are not available, contact Task Manager for authorization to proceed. Authorization to proceed:

Yes_____No_____

Date_____Time_____Task Manager _____)

Selection of sampling points and time according to methodology? _____

Number of sample points_____Sample time/point_____

Minimum sample volume required?_____

Minimum run time required? _____

Total sample time actual? _____

Sampling train assembled properly? _____

Filter properly centered?_____Impingers properly charged? _____

Number of impingers required? _____

Sample train preparation (Volume added to each impinger):

1st (normally empty)_____

2nd/3rd (100 mL of HNO_3/H_2O_2) _____

4th (normally empty)_____

5th/6th (100 mL of permanganate solution) _____

(Note: Reagent prepared fresh daily? _____

7th (200-300 g of preweighted silica gel) _____

Weight (Initial) _____

Pitot tube lines checked for plugging or leaks? _____

Stopcock grease used: Acetone-insoluble?_____Heat-stable?_____

Meter box leveled?_____Manometers leveled? _____

Probe heat uniform along length of probe?_____

Dry gas meter field observation check:

A. Operating Meter Box Assembly

Operate metering system for 10 minutes at the H@ value. Record the volume metered, DGM temperature and barometric pressure.

Final: DGM reading_____ft^3 Temp_____ °F P_b_____ in. Hg
Initial: DGM reading_____ft^3 Temp_____ °F P_b_____ in. Hg
Net: V_m = _____ft^3 Avg. T_m = _____ °F + 460 = _____

$Y_c = 10/V_m [0.0319 (T_m = 460)/P_b]^2$ = _____
$Y_c = 0.97\ Y = 1.03\ Y$ = _____

Criteria: $0.97\ Y < Y_c < 1.03\ Y$; System meets?_____ Exceeds? _____

B. Utilizing EPA's Method 5 Dry Gas Meter Performance Test Device

a. Remove the performance test device from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box..
b. Turn the power to the meter box on and start the pump.
c. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading.
d. Allow the orifice and source sampling meter box to warm up for 45 minutes with flow controls adjusted as described in step c before starting quality assurance runs.
e. Make triplicate quality assurance runs. For each run, record initial and final dry gas meter volume, dry gas meter inlet and outlet temperatures, internal orifice pressure drop (Delta H), ambient temperature, and barometric pressure. Each run duration should be greater than 15 minutes. As the needle reaches the zero (12 o'clock) position, the pump and stopwatch are stopped simultaneously. The dry gas meter volume and time are recorded.

QA Table For Evaluating DGM Orifice Value

Item	Run 1	Run 2	Run 3
DGM, final			
DGM, initial			
DGM, net			
DGM, T inlet (°F)			
DGM, T outlet (°F)			
DGM, T avg (°F)			
Ambient Temp. (°F)			
Pb (in. Hg)			
Orifice meter, Delta H			

f. Calculate the corrected dry gas volume for each run using the following equation: .

$Y_c = 10/V_m [\ 0.0319\ (T_m = 460)/P_b]^2 =$ _____
$Y_c = 0.97\ Y = 1.03\ Y =$ _____
Criteria: $0.97\ Y < Y_c < 1.03\ Y$; System meets?_____ Exceeds? _____

Nomograph/calculator check:

a. Nomograph:

If Delta H@ = 1.80, T(meter) = 100 F, % moisture = 10 %, Ps/Pm = 1.00, calculate C.

C = _____ (0.95)

If C = 0.95, T_s = 200 F, D_n = 0.375, Delta p reference = _____(0.118)

Align Delta p = 1.0 with Delta H = 10; and lock nomograph. Set p = 0.01.
Read Delta H_____ (0.01)
Nomograph O.K.? _____

b. Calculator:

Calculate Delta H/delta p using the following equation:

$$\text{Delta H/Delta p} = \{846.72\, D_n^4 [\text{Delta H@}]\, Cp^2\, (1-B_{ws})^2 (M_d T_m P_s / M_s T_s P_m)\}$$

= _____
= _____
= _____

Parameters for calculator check:

Item	Dimensions	Given	Calculated
A. Orifice meter coefficient, Delta H@	in. Water	1.80	_____
B. Pitot tube coefficient, Cp	dimensionless	0.84	_____
C. Abs. stack pressure, $P_s = P_b + P_{st}$	in. Hg	29.96	_____
D. Abs. meter pressure, P_m +/- P_b	in. Hg	29.92	_____
E. Abs. meter temperature, $T_m = t_m + 460$	degrees R	560	_____
F. Abs. stack temperature, $T_s = t_s + 460$	degrees R	760	_____
G. Dry molecular weight, M_{wd}	lb/lb-mole	30	_____
H. Moisture content, B_{ws} + % water/100	dimensionless	0.10	_____
I. Exact nozzle diameter, D_n	in.	0.375	_____
J. Average velocity head, Delta p	in. Water	0.1	_____
K. K factor = Delta H/Delta p		13.24(	_____)
L. Delta H calculated for delta p = 0.1	in. Water	1.324(	_____)

Calculator equation set-up O.K.? _____

Nomograph /calculator setup:

A. Delta H@ = _____
B. C_p = _____
C. P_s = _____
D. P_m = _____
E. T_m = _____
F. T_s = _____
G. M_d = _____
H. % M = _____
I. C Factor = _____
J. D_n desired = _____ in. Actual _____ in..
K. Avg. Delta p = _____
L. Delta H calculated = _____

Nomograph set up O.K.? _____
Calculator set up O.K.? _____
K-factor figured properly? _____

Care taken to avoid scrapping nipple or stack wall?_____
Effective seal made around probe when in-stack? _____
Pretest leak check performed? _____
Probe moved at proper time? _____
Pitot tube/probe marking correct for correct sampling points?_____
Nozzle and pitot tube parallel to stack wall at all times? _____
Filter changed during run? _____
Any particulate loss during changing? _____
Leak check before changing components during run? _____
Data sheets completed, in ink, and data properly recorded?_____
Percent isokinetics calculated at each point?_____Within 90-110 %? _____
Perform % isokinetic rate check:

Delta H/Delta p = $\{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_dT_mP_s/M_sT_sP_m)\}$ =
K-factor changed during run? _____
New K-factor_____
Velocity pressures and orifice pressure readings recorded accurately? _____
Post-test leak check performed?(Mandatory) _____
Leakage rate_____@ in. Hg_____
If data sheets cannot be copied, record approximate stack temperature, average stack velocity delta p, average stack delta H, approximate stack gas moisture, approximate dry stack gas molecular weight, nozzle diameter, pitot tube coefficient. Gas density determination: Temp. sensor type_____ Pressure gauge _____
Temperature sensor attached to probe?_____Other _____

Recovery:

Construction of probe recovery brushes: Nylon_____Clean_____Other_____
Wash bottle: Clean/glass?_____
Storage containers: Borosilicate glass?_____Other_____Clean?_____
Leak free?_____Teflon-lined caps? _____
Petri-dishes: Glass?_____Polyethylene_____Other_____Clean? _____
Graduated cylinder/or balance: Subdivisions </= 2 mL?_____Other_____
Balance type?_____Calibrated? _____
Plastic storage containers: Air-tight?_____Clean?_____
Probe allowed to cool sufficiently?_____
(Note: Cap placed over nozzle tip to prevent loss of particulate matter?(_____)
During sampling train disassembly, are all openings capped? _____
Clean-up area: Description _____

Clean-up area clean and protected from wind?_____
Sample recovery:
Container No. 1 (Filter):
Filter handling: Polypropylene tweezers used?_____
Surgical gloves worn?_____Other _____
Any particulate matter spilled?_____

Container No. 2 (Probe rinse/acetone):

Acetone rinse?_____Distilled water rinse? _____
Probe nozzle?_____Probe fitting? _____
Probe liner?_____Front half of filter holder? _____
Fluid levels properly marked?_____

Container No. 3 (Probe rinse/ 100 mL nitric acid)

Exactly 100 mL of nitric acid used? _____
Probe nozzle?_____Probe fittings? _____
Probe liner?_____Front half of filter holder? _____
Fluid levels properly marked?_____
Any visible particles or permanganate solution (brown color) on filter holder or inside probe?

Container No. 4 (Impingers 1 through 3):

Liquids measured volumetrically to within 0.5 mL? _____
Liquids in one or several containers? _____
Impingers, back half of filter housing, connecting glassware rinsed withexactly 100 mL of 0.1 M nitric acid?_____
Fluid levels properly marked?_____

Container No. 5A (Normally empty impinger 4):

Liquid measured volumetrically to within 0.5 mL? _____
Impinger rinsed with exactly 100 mL of 0.1 M nitric acid? _____
Fluid levels properly marked?_____

Container No. 5B (Impingers 5 and 6 containing permanganate solutions):

Permanganate solution color?_____
Spent (Complete bleaching of purple color)? _____
Liquid measured volumetrically to with 0.5 mL?_____
Impingers rinsed with freshly prepared 100 mL permanganate sol.? ___
Impingers rinsed with 100 mL reagent water? _____
Fluid levels properly marked?_____
(Note: Bottles should not be filled completely to allow venting.)

Container No. 5C (Rinsing of impingers 5 and 6 with 8 M HCl):

200 mL reagent water added to Container No. 5C? _____
Exactly 50 mL of 8 M HCl used to rinse impingers 5 and 6?_____
Fluid level properly marked? _____

Container No. 6 (Impinger 7 containing silica gel):

Color of recovered silica gel? _____
Method of silica gel transferred? _____
Silica gel weighted to nearest 0.5 g?_____
Container properly labeled/sealed?_____

Container No. 7 (Acetone blank):

100 mL placed in Container 7?_____
Fluid level properly marked? _____
(Note: If particulate matter is not being determined, then an action lank is not necessary.)

Container No. 8A (0.1 M nitric acid blank):

300 mL of 0.1 M nitric acid used in sample recovery placed in Container 8A? _____

Fluid level properly marked? _____

(Note: Need only one blank per field test.)

Container No. 8B (Reagent water blank):

100 mL of reagent water blank placed in Container 8B? _____

Fluid level properly marked? _____

(Note: Need only one blank per field test).

Container No. 9 (Nitric acid impinger reagent blank):

200 mL of nitric acid impinger reagent placed in Container 9? _____

Fluid level properly marked? _____

(Note: Need only one blank per field test).

Container No. 10 (Permanganate reagent blank):

100 mL of permanganate impinger reagent placed in Container 10? ___

Fluid level properly marked? _____

(Note: Need only one blank per field test).

Container No. 11 (8M HCl blank):

200 mL of reagent water placed in Container No. 11? _____

25 mL of 8 M HCl placed in Container No. 11? _____

Fluid level properly marked? _____

(Note: Need only one blank per field test).

Container No. 12 (Filter blank):

Unused filter from same lot of field filter placed in Container No. 12? _

_____

Petri dish sealed? _____

All jars adequately labeled? _____

Jars sealed tightly? _____

Liquid level marked on jars? _____

Jars locked up and chain-of-custody completed? _____

Teflon tape used to secure seal of jars? _____

All data forms signed and chain-of-custody completed? _____

Gas sample volume corrected to standard temperature and pressure? _____

Remarks _____

_____

STACK TESTING FOR HAZARDOUS AIR POLLUTANTS (HAPs)

FIELD OBSERVATION CHECKLIST

SW-846, METHOD 0061

DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS FROM STATIONARY SOURCES

SOURCE INFORMATION

Facility_____ Location _____
Source_____ Sampling _____
Location _____
Test Team_____Team Leader_____
Test Date Interval:_____/_____/_____ to _____/_____/_____
Observer_____Affiliation_____

PRETEST MEETING CHECKLIST

Please reference Pretest Checklist.

FEDERAL REFERENCE METHODS 1 THROUGH 5

Please reference Federal Reference Methods 1 through 5 Checklist

SW-846, METHOD 0061

DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS FROM STATIONARY SOURCES

Equipment identified matches pretest calibration list? _____
Train Design: Recirculating train where the impinger reagent is continuously recirculated to the nozzle. Aspirator design? _____Pump/Sprayer design?_____

Apparatus:

NOZZLE

Probe nozzle: Glass/Teflon (Required)_____Other _____
Probe design: Button-hook _____Elbow _____Other _____
Nozzle size:_____Calculated_____Measured three times _____
Nozzle condition: Nicks/Chips_____

PROBE/PROBE LINER

Probe material: Glass/Teflon (Required) _____

Criteria: 0.97 Y < Y_c < 1.03 Y; System meets?_____ Exceeds _____

B. Utilizing EPA's Method 5 Dry Gas Meter Performance Test Device

a. Remove the performance test device from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box.
b. Turn the power to the meter box on and start the pump.
c. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading.
d. Allow the orifice and source sampling meter box to warm up for 45 minutes with flow controls adjusted as described in step c before starting quality assurance runs.
e. Make triplicate quality assurance runs. For each run, record initial and final dry gas meter volume, dry gas meter inlet and outlet temperatures, internal orifice pressure drop (Delta H), ambient temperature, and barometric pressure. Each run duration should be greater than 15 minutes. As the neddle reaches the zero (12 o'clock) position, the pump and stopwatch are stopped simultaneously. The dry gas meter volume and time are recorded.

QA Table For Evaluating DGM Orifice Value

Item	Run 1	Run 2	Run 3
DGM, final			
DGM, initial			
DGM, net			
DGM, T inlet (°F)			
DGM, T outlet (°F)			
DGM, T avg (°F)			
Ambient Temp. (°F)			
Pb (in. Hg)			
Orifice meter, Delta H			

f. Calculate the corrected dry gas volume for each run using the following equation:

$Y_c = 10/V_m [\ 0.0319\ (T_m = 460)/P_b]^2 =$ _____

$Y_c =$ _____

$0.97\ Y =$ _____

$1.03\ Y =$ _____

Criteria: $0.97\ Y < Y_c < 1.03\ Y$; System meets?_____ Exceeds? _____

Nomograph/calculator check:

a. Nomograph:

If Delta H@ = 1.80, T(meter) = 100 F, % moisture = 10 %, Ps/Pm = 1.00, calculate C.

C = _____ (0.95)

If C = 0.95, T_s = 200 F, D_n = 0.375, Delta p reference = _____(0.118)

Align: Delta p = 1.0 with Delta H = 10; and lock nomograph. Set p = 0.01.
Read Delta H_____ (0.01)
Nomograph O.K.?_____

b. Calculator:

Calculate Delta H/delta p using the following equation:

$$\text{Delta H/Delta p} = \{846.72\ D_n^4[\text{Delta H@}]\ Cp^2\ (1-B_{ws})^2(\ M_d T_m P_s / M_s T_s P_m)\}$$

= _____
= _____
= _____

Parameters for calculator check:

	Item	Dimensions	Given	Calculated
A.	Orifice meter coefficient,	Delta H@ in. Water	1.80	_____
B.	Pitot tube coefficient,	Cp dimensionless	0.84	_____
C.	Abs. stack pressure, $P_s = P_b + P_{st}$	in. Hg	29.96	_____
D.	Abs. meter pressure, P_m +/- P_b	in. Hg	29.92	_____
E.	Abs. meter temperature, $T_m = t_m + 460$	degrees R	560	_____
F.	Abs. stack temperature, $T_s = t_s + 460$	degrees R	760	_____
G.	Dry molecular weight, M_{wd}	lb/lb-mole	30	H. Moisture content, B_{ws} + % water/100 dimensionless 0.10 _____
I.	Exact nozzle diameter, D_n	in	0.375	_____

Container No. 6 (0.1 M nitric acid blank):

Equal volume placed in Container No. 6 used to rinse sample train? _____

(Note: Need only if total chromium is being measured and only one blank per field test.)

Fluid level properly marked? _____

All jars adequately labeled? _____

Jars sealed tightly?_____Liquid level marked on jars? _____

Jars locked up and chain-of-custody completed? _____

Teflon tape used to secure seal of jars?_____

All data forms signed and chain-of-custody completed? _____

Gas sample volume corrected to standard temperature and pressure? _____

Remarks: _____

_____

_____

_____

Appendix E

Sampling and Analysis For HAPs Under Title III of the CAAA of 1990 (Stack Test Methodologies)

Sampling and Analysis
For Hazardous Air Pollutants (HAPs)
Under Title III of the Clean Air Act Amendments
Of 1990
(Stack Test Methodologies)

Larry Johnson (Retired)
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

William T. "Jerry" Winberry, Jr.
EnviroTech Solutions
1502 Laughridge Drive
Cary, North Carolina 27511
Email: jwinberry@mindspring.com

I. INTRODUCTION

Over the last several years, public awareness of air pollution and its sources has increased steadily. Specifically, since the passage of the Clean Air Act Amendments of 1990 (the Act), more emphasis has been placed on local, State, and Federal agencies to keep the public informed on health effects of various air toxics and levels of exposure. This awareness has required industry to become accountable for air toxics emission as part of a source's compliance strategy.

Title III of the Act, Hazardous Air Pollutants (HAPs), mandates that EPA address emissions of HAPs from both area and point sources. Provisions within Title III require EPA to categorize sources, regulate emissions of 189 hazardous air pollutants, determine applicability of maximum achievable control technology (MACT), evaluate residual risk after MACT, and address sudden accidental releases.

The timetable to meet the above provisions has begun for EPA. In addition, States will soon impose entirely new operating permit requirements. The Amendments require that State programs include a standard application form and monitoring and reporting requirements, along with annual fees. Permits will be valid for no more than 5 years, each with specific emission limits and a source specific compliance schedule.

In this new era of environmental awareness, industry must be prepared to know exactly what is being emitted from its facilities. the availability of quantitative source specific emission data long with risk information enables an industry to respond correctly to federal and State regulatory initiatives.

This is a second part of a two-part article involving sampling and analysis for HAPs as a result of Title III of the Act. Part I dealt with ambient methodology for the characterization of HAPs. This article, Part II, will discuss standardized sampling and analytical methodology used by EPA for quantifying HAPs emissions from point sources. The use of standardized test procedures will ensure compatibility of the data collected with its ultimate use as part of an industry emission monitoring program.

II. CLEAN AIR ACT AMENDMENTS OF 1990

Under Title III of the Act, EPA has listed 189 hazardous air pollutants. In general, sources that emit more than 10 tons per year of any listed substance or 25 tons per year of any combination of listed substances must limit the emissions of these HAPs and comply with the provisions. Approximately 250 source categories will be affected.

The standards for listed source categories will require MACT as a means of reduction in emissions. For existing sources, the applicable standard must at least achieve control levels to within 12% of the most tightly controlled existing sources. Existing sources must comply within three years of established MACT standards. For new sources, the standards must be more stringent than for existing sources. For both new and existing sources, technology feasibility and cost are factors which EPA must consider in determining maximum achievable controls.

Under some circumstances, MACT may not be sufficient to assure public health protection or may produce significant environmental impacts. If any significant residual risk remains, EPA must tighten the emission reductions. The residual risk standards must be applied to assure an "ample margin of safety" to protect human health and protect the environment. These standards must be set by EPA for pollutants which may cause cancer whenever the risk is greater than 1-in-1,000,000 to the MEI (maximum exposed individual).

The sudden accidental release section of the Act requires owners and operator of facilities which handles extremely hazardous substances to operate safely. It also requires an engineering analysis of the facility to identify potential hazards to public health. The Act establishes a Chemical Safety Board to investigate accidents and requires EPA to promulgate accident prevention regulations

All of the above regulatory initiatives will require sources to quantitate their emissions in order to demonstrate compliance. Similar to ambient methodology, EPA has published numerous sampling and analytical methods for quantifying HAPs from industrial sources. Within the EPA, different programs have required the development of standardized methods involving different matrices to meet program objectives. The development of standardized methods has been initiated in most cases by regulatory mandates to support specific programs. Methods may therefore be found within the legislative announcement (i.e., Federal Reference Methods) or referenced to a particular compilation (i.e., Compendium of Methods, Statement-of-Works, EPA publications like SW-846, etc.) of analytical methodology.

III. FEDERAL REFERENCE METHODS (FRMs)

Regulatory authority associated with the enforcement of air quality standards has its basis in the Clean Air Act and its amendments. The Clean Air Act Amendments of 1970 established the Environmental Protection Agency, which was given the mandate to set and enforce the regulations. k became the responsibility of EPA to "*protect and enhance the quality of the Nation's air resources so as to promote the public health* and *welfare and the productive capacity of its population...*" It is within this time frame that Federal Reference Methods were established to be used as regulatory methodology in determining compliance by both the Agency and the affected facility. In 197 I, the original eight FRMs were promulgated (36 FR 24877) dealing with stack gas monitoring. Since that time, FRMs have been developed to support major EPA programs dealing with New Source Performance Standards NSPS), Prevention of Significant Deteriation (PSD) and National Emission Standards for Hazardous Air Pollutants (NESHAPs), to name only a few. FRMs are methods developed in some cases for a specific source category to demonstrate compliance with an applicable standard.

As an example, FRM 16 is identified as one of the compliance methods for Subpart BB, Kraft Pulp Mills, but has also been used for monitoring total reduce sulfur (TRS) emissions from refineries, hazardous incinerators and other sources not originally intended when proposed in the regulations. Consequently, FRMs were designed with a specific need in mind for determining compliance with a pollutant emission limit. With the passage of the Act, Title III forced the Agency to look for test methodology which could quantitate many constituents at a time, thus reducing cost for an industrial source compliance program.

IV. SW-846: TEST METHODS FOR EVALUATING SOLID WASTE: PHYSICAL AND CHEMICAL METHODS

The U. S. EPA's Office of Solid Waste (OSW), under the authority of the Resource Conservation and Recovery Act (RCRA), has developed a Compendium of test and analytical methods for use in determining regulatory compliance under RCRA. The title of the Compendium is *"Test Methods for Evaluating Solid Waste (SW-846)."* Except where mandated, SW-846 serves as a guidance document outlining criteria of acceptance in response to RCRA regulatory initiatives.

While the original intent of SW-846 was to address solid waste, it has been expanded to now include sampling and analytical methods associated with both ambient and source monitoring. This is due, in part, to the public outcry for EPA to monitor not only the water and soil pathways at hazardous waste sites utilizing incinerators as the method of destruction, but also to monitor the air pathway from the incinerator emissions in order to demonstrate compliance with national, state and local standards.

SW-S46 was conceived around 1980. Since that time, there have been several updates. The present regulatory status of the Compendium requires the use of the Third Edition methods (including Updates).

The basic question most frequently asked associated with SW-846 methods is: *"Are they EPA approved?"* Mr. Lesnik answered that question in his article entitled: *"Additional Perspective on SW-846. How and When Can Draft Methods Be Used?"* In that article, he states: *"U. S. EPA approval means that a method has been incorporated by reference in a Final Rule that has been published as a Federal Register Notice (FRN) either into SW-846 or directly into the RCRA regulations. In short, U. S. EPA-approved methods are promulgated methods that can be used without special permission for RCRA applications for which the use of SW-846 methods is mandatory". Therefore, until a method is promulgated by an* FRN, it *is not an approved method for these mandatory applications, no matter where it may be in the regulatory process."*

SW-846 methods are not published in the *Federal Register,* but are incorporated by reference in the appropriate RCRA regulations.

The present source test methods found in SW-846 were actually funded and developed by EPA's Office of Research and Development (ORD) through the Atmospheric Research and Exposure Assessment Laboratory (AREAL). Methods found in SW-846 have never been published in the *Federal Register* as reference methods.

V. SOURCE METHODOLOGY

Dr. Larry Johnson's article entitled: *"Testing The Air: The Basics and Beyond,"* discussed two of the methods found in SW-846: Method 0010 (Modified Method 5) and Method 0030 (Volatile Organic Sampling Train [VOST]). Both of these methods have been used to characterize over eighty-five percent (85%) of the Title III HAPs. Following is an overview of other SW-846 source test methods which are applicable to quantifying Title III HAPs emissions from industrial sources. Our discussion will address the following methods:

- Method 0010: Condensible Organic Compounds;
- Method 0011: Formaldehyde Emissions;
- Method 0030: Volatile Organic Compounds;
- Method 0050: Particles and HCl/Cl_2; and
- Method 0060: Multiple Metals Train.

Semi-volatile (Condensible) Organic Compounds (SW-846 Method 0010)

Semi-volatile (condensible) organic compounds from hazardous waste incinerators are determined utilizing Modified Method 5 (MM5) sampling train. The MM5 protocol is outlined as Method 0010 in SW-846, **"Test Methods for Evaluating Solid Waste,"** Third Edition, November 1986. The sampling train consists of a heated probe, heated filter, sorbent module, pumping and metering unit. A gooseneck nozzle of an appropriate diameter to allow isokinetic sample collection is attached to the probe. An S-type pitot tube is used to monitor the velocity pressure and an orifice meter is used to determine the isokinetic sampling rate. From the heated filter, sample gas enters the sorbent module. The sorbent module consists of a water-cooled condenser followed by an XAD-2 resin trap. Following the resin trap is a dry, modified Greenburg-Smith impinger which collects the aqueous condensate. The stem of this impinger is short to reduce carryover of collected aqueous condensate. Following the condensate trap are two dry impingers to collect any mist carryover from the condensate trap and a final impinger containing silica gel to dry the sample gas before metering. A pump and dry gas meter are used to control and monitor the sample gas flow rate.

Samples extracted from hazardous waste incinerator stacks using SW-846 Method 0010 sampling procedures are analyzed for condensible organic compounds using Soxhlet extraction followed by low resolution capillary column GC/MS in accordance with Method 8270 found also in SW-846. The method uses matrix specific extraction and analyte specific cleanup techniques for sample preparation. Stack gas samples collected by the Modified Method 5 sampling train are extracted with methylene chloride. The extracts are then acid-base washed, purified and concentrated for analysis by GC/MS. Calibration of the GC/MS is accomplished with internal standards and calibrating solution.

Volatile Organic Compounds (SW-846 Method 0030)

Volatile organic compounds from hazardous waste incinerators are determined utilizing the volatile organic sampling train (VOST). The VOST is described in Method 0030 in SW-846, **"Test Methods for Evaluating Solid Waste,"** Third Edition, November 1986.

The VOST was designed to quantitatively determine volatile principle organic hydrocarbons (POHCs) and other hazardous substance list (HSL) volatile organics present in the flue gas of incinerators to be used in calculating destruction removal efficiency (DRE). The method utilizes Tenax. and Tenax./Charcoal cartridges to adsorb the volatile organic compounds; each cartridge is preceded by a condensing module.

The train consists of a glass-lined probe with a glass wool plug to remove particulate, followed by an assembly of condensers and organic resin traps. The first condenser cools the gas stream and condenses the water vapor present. The flue gas moisture is collected in the first impinger which is continually purged by the gas stream. The second condenser cools the gas stream further and the gas enters the second sorbent trap to prevent breakthrough of the target compounds. Following the second sorbent trap is a silica gel drying tube for residual moisture removal. Approximately 20 liters of sample gas is collected on each pair of traps with a 1.0 liter sampling rate to give a nominal 20-minute sampling period.

Analysis of the sorbent traps are performed by a "purge-and-trap" configuration, as specified in Method 5040 of SW-846.

Upon receipt at the laboratory, the content of the sorbent traps (Tenax and Tenax./Charcoal) are spiked with an internal standard. The sorbents are then thermally desorbed for 10 minutes at 180°C with organic free nitrogen on helium gas (at 40 mL/min), bubbles through 4 mL of organic free water, and then trapped on a second (analytical) adsorbent trap.

The analytical adsorbent trap is rapidly heated to 180°C following the 10 minute desorption, and the carrier gas flow is reversed so that the effluent flow from the analytical trap is directed into a GC/MS. Volatile compounds are then separated by temperature programmed gas chromatography and detected by low-resolution mass spectroscopy as outlined in Method 8240 of SW-846.

Aldehydes and Ketones (Formaldehyde) Emissions (Method 0011)

Aldehydes and ketones (especially formaldehyde) are determined using a Federal Reference Method 6 sampling train involving midget impingers. The Method is described in SW-846 Method 0011 in SW-846, **"Test Methods for Evaluating Solid Waste,"** Third Edition, November 1986. Method 0011 is used to determine the destruction and removal efficiency (DRE) of formaldehyde. Although this methodology has been applied specifically to formaldehyde, many laboratories have extended the application to other aldehydes and ketones. Compounds derivatized with 2,4-dinitrophenylhydrazine (DNPH) can be detected in concentrations as low as 6.4×10^{-5} lbs/cu ft (1.8 ppbv) in 40 cu fit of stack gas sampled over a 1-hour period. Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic DNPH solution. Formaldehyde (and other aldehydes and ketones) present in the emissions reacts with DNPH to form the dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography (HPLC).

Multiple Metals Emissions (Method 0060)

The determination of metal emissions from hazardous waste incinerators involves a modification of the Method 5 train. The sampling train is operating as a Method 5 particulate train with modifications to the impinger configuration to enhance the collection of metals of interest. The train is described in Draft Method 0060 in SW-846, **"Test Methods for Evaluating Solid Wastes,"** Third Edition, November 1986. The method has been utilized for the collection of the following metals: antimony, arsenic, barium, beryllium, cadmium, chromium (total), lead, mercury, silver and thallium.

A thermocouple and S-type pitot tube are attached to the probe for measurement of gas temperature and velocity. Sample gas is drawn through the nozzle and probe and then through a heated quartz fiber filter (250°F+25°F). Particulate collected on the filter and in the probe will be weighed and analyzed for the metals of interest.Upon exiting the filter, the gas is drawn through a series of six impingers designed for collection of volatile metals including mercury. The contents of the second and third impingers are analyzed for all metals with the contents of the 4th, 5th, and 6th impingers analyzed for only mercury. Following the impinger system, the gas is drawn through a dry gas meter, a calibrated orifice and a leak-free oil fiber vane pump. This method is basically an EPA Method 5 sampling train with some very specific modifications:

1) The nozzle and probe liner is glass or quartz with all connections glass or Teflon;
2) The filter is glass or quartz, with a fritted glass support;
3) Impingers 1 and 2 contain a 5% nitric acid (HNO_3) and 10% hydrogen peroxide (H_2O_2) solution;
4) Impinger 3 contains a 4% potassium permanganate ($KMnO_4$) and 10% sulfuric acid (H_2SO_4) solution;
5) Impinger 5 is dry and is followed by an impinger containing silica gel desiccant; and
6) A non-metallic brush and 0.1 N nitric acid is used for the probe and nozzle rinse.

Impinger solutions and probe rinses are analyzed by inductively coupled argon plasma emission spectroscopy (ICPES), atomic absorption spectroscopy (AAS), or graphite furnace AAS depending upon sensitivity required or the matrix effects on the specific analyte.

To sample chromium (Cr^{+6}), a modification to the multiple metals train is used. This is SW-846 Method 0061. The difference between the trains is the use of recirculating impinger fluid. This method can be found in "Methods Manual for Compliance with the BIF Regulations," EPA 503-SW-91-101, December 1990.

HCl/$C1_2$ (Method 0050)

Sampling for the HCl/$C1_2$ and particles associated with HCl/Cl_2 from hazardous waste incinerators can be determined together utilizing Method 0050. The method is described In Method 0050 in SW-846, **"Test Methods for Evaluating Solid Wastes,"** Third Edition, November 1986.

Method 0050 is an isokinetic method involving the Method 5 sampling train, where six (6) impingers and used, instead of the traditional four (4) impingers. The 1st impinger is a knock-out impinger, with the 2nd and 3rd impingers containing 0.1N H_2SO_4 solution and the 4th and 5th impingers containing 0.1N NaOH solution for more effective collection of HCl and Cl_2. The 6th impinger contains silica gel.

A minimum of 30 dscf of stack gas is collected over a minimum 3-hour period. The guidelines presented in EPA Method 1 are used to determine the number of sampling points required across the diameter of the stack for measuring the average stack gas velocity and particulate loading.

At the end of the sampling period, the nozzle, probe liner, and glassware preceding the filter are rinsed with deionized water and acetone to remove particulate matter from the probe assembly. These washings are collected, evaporated to dryness, and the mass of any residual particulates determined gravimetrically. The glass fiber filter is desiccated and then weighed to determine the mass of filtered particulates. The total particulate mass from the filter and probe wash are divided by the total volume of gas sampled to determine the front half particulate loading.

The moisture content of the stack gas is determined by the total weight gain of the impingers used over each Method 0050 sampling period. HCl is determined by analysis of the first three impinger solutions combined, using ion chromatography. $C1_2$ is determined by analysis of the 4th and 5th impinger solutions combined, using ion chromatography.

VI. HAPs TARGET SAMPLING/ANALYTICAL METHOD SELECTION USING SW-846 METHODOLOGY

When a sampling and analytical methodology is selected for a given analyte or group of analyses, the first priority should be given to the use of existing *Federal Register* methods (40 CFR Parts 60 and 61) which have been validated specifically for the analyses of interest in stationary sources. These methods have documented precision and accuracy associated with them. Methods also found in EPA's SW-846, **"Test Methods for Evaluating a Solid Waste" and "Methods Manual for Compliance with BIF Regulations"** should be considered part of this level of highest accuracy and precision and should be used when quantifying emissions from hazardous waste incinerators. It is the intent of EPA and its ultimate goal to have validated test methods for all listed 188 HAPs under Title III of the CAAA of 1990.

Based upon EPA's years of experience and diligent work of its contractors, Table 1 contains suggested source methodology for sampling and analysis of the HAPs listed in Title III of the Act utilizing SW-846 methodology. The methods were selected based upon:

- Validation data available from consultants and vendors;
- Availability and reliability of sampling and analytical methodology for selected analytes; and
- Applicability of the selected methodology to a wide range of analytes.

Table 1is not comprehensive. Many of the methods selected were based upon years of experience utilizing the methodology and having that feeling that **"the method should work for this compound if it worked for another."**

It is anticipated that many of the sampling and analytical procedures recommended need additional development and validation efforts to improve accuracy and precision. It should be stressed that a method which requires validation is not an inferior method; the method simply requires

additional experimentation to define precision and bias. The performance of the method for a given analyte and source may be entirely acceptable, but until validation data are available, the use cannot know that the performance of the method will be acceptable prior to use.

To validate a method for a given analyte, the following procedures must be performed:

- A known concentration of an analyte must be introduced in the sampling procedure and carried through the entire sampling and analytical procedure to assess the bias of the proposed method;
- Alternatively, the proposed test method may be compared against a previously validated test method in order to assess bias; and
- Multiple or collocated simultaneous samples must be collected to determine the precision of the test method.

For those methods that do not have accuracy and precision data associated with them, EPA Method 301 should be used. Method 301 procedures determine bias (systematic error) and precision (random error) of a test method at a permissible emission concentration, e.g., emission standard, in the gas stream. The procedures in Method 301 involve (a) introducing known concentrations of an analyte or comparing the test method against a validated test method to determine the method's bias and (b) collecting multiple or collocated simultaneous samples to determine the method's precision.

Table 1 should be useful to those individuals who must assist with the selection of sampling and analytical methods to quantitate the Title III HAPs. However, several caution notes must be given when using Table 1. They are:

- Table 1 contains a summary of the methods type and status for stack sampling and analysis of each of the 188 air toxics listed in the 1990 Clean Air Act Amendments. Table 1 have no direct regulatory standing, and therefore do not constitute approval of the use of the methods to satisfy regulatory requirements. Such approval must always be obtained from the regulatory agency or group involved in the individual project. Hopefully this compilation will aid both the regulator and the regulated community in making planning decisions for air toxics source testing.

- A large amount of field evaluation data has been produced by EPA and its contractors since 1989, and an attempt has been made to utilize all of it in Table 1. Table 1, therefore, is based on field and laboratory test information. No attempt has been made to perform a comprehensive literature survey and to include field test information from sources outside EPA. It is the author's opinion, however, that very little data from outside sources exists that would meet the criteria needed for useful inclusion in this table. Footnotes for each column in Table 1 lead the reader to a corresponding item on the Reference List. The reference list contains at least one source, usually a report and a paper, for all of the recently generated data and for some of the older studies.

- Methods such as 0010 (MM5), 0030 (VOST sampling), 5041/8260 (VOST analysis), and 8270 (GC/MS) are from the SW-846 Methods Manual used by EPA's Office of Solid Waste (OSW) and the Regions for RCRA related work. Method 5, Method 15, and Method 106 are examples of Federal Register Methods historically related to OAQPS air programs. Some of the methods have been promulgated by both groups under different method numbers. Methods and other useful material can be obtained from sources given later in this document. The SW-846 methods listed are the most recent versions, for example 8270C and 5041A. In the future, later versions of the same method should function just as well, or better. In most cases, data obtained with earlier versions of the same method will also be sound, but new tests should always utilize the most recent rendering of the procedure. Methods such as XHCN and XACN are Office of Research and Development produced methods which have been cleared for publication, but which have not yet been promulgated by one of the program offices. Copies of the "X" methods are included in the corresponding research reports listed in the references.

- The sampling methods listed are generally intended for relatively low concentrations of materials in stack gases. Alternate methods may be necessary for process streams or flue gases with no control devices. Not all methods that might be effective are included on the table. The Tedlar bag version of Federal Reference Method 18 would probably be effective for the same compounds that 0040 sampled well, provided that the source did not emit particulate matter or condensable water vapor, and that sorption losses in the lines were minimal. The performance of the sorbent tube version of Federal Reference Method 18 would be less easy to predict, and would have little relation to 0040 performance.

- Priority has been given in Table 1 to methods such as 0010 (i.e., Modified Method Five, Semi-VOST) or Method 29/ Method 0060 (i.e., the Multiple Metals Train) which have the most potential for determination of many compounds or metals simultaneously. Alternate single pollutant methods are often given in the comments column. Exclusion of a method from Table 1 does not necessarily imply that it will not perform adequately.

- Many of the compounds on this list are also on RCRA Appendix 8 but listed under a different name. In cases where common, alternate identities have been identified, these are given in the comments column. No attempt has been made to list all alternate chemical names. In some cases, two inconsistent chemical names or an inconsistent pairing of a name with a CAS number has been given on the CAAA list. Cases such as these have been noted in Table 1, and the CAS number has been assumed to be the primary reference (i.e. the correct CAS number for the compound intended to be regulated). The authors have no idea, whatever, what the legal ramifications are of such mistakes in the CAAA.

- In general, the compounds that have identical listings in the sampling column and in the analysis column can be determined simultaneously. Some of the analyses may require more than one GC or HPLC run to accomplish this end.

- Unless otherwise stated, metals methods produce total Cr, total Pb, etc. Metals oxidation state or compound speciation is always difficult, often impossible, and requires special sampling and analytical options.

- Even though much less field data is available for Method 0031 than for Method 0030, the former should always perform at least as well as the latter, and often times better. The limited comparison data generally, but not always, supports this position. The authors believes that 0031 can always be successfully substituted for M0030, and usually should be chosen for new projects.

- Only CAAA toxics are included in Table 1.

- Poor performance of one of the basic methods such as M0010 is often a result of reactivity of the target compound. The relatively non-reactive compounds will consistently show good recoveries, the highly reactive compounds will consistently exhibit very poor recoveries, but the marginally reactive compounds may show variability as a function of the reactivity of the stack gas matrix being sampled. Cloroprene, for example, yielded field test results of f2 and f4 along with l1 laboratory recoveries. Caprolactam actually showed f1, f4, and l1 results. When sampling compounds with a history of mixed performance, it is probably a good idea to spike the sorbent resin (for sorbent methods) with an isotopically labeled recovery standard before sampling. Carbon or chlorine labels are the least likely to exchange to another compound. Method 23 uses a form of this technique, as does M0040.

- Laboratory recoveries are not usually shown in Table 1 unless field results were poor, or the laboratory results are at odds with the field results. The code does not indicate how many field results of a given category were obtained.

- A number of the CAAA compounds were eliminated from further testing with Methods 0030 and 0010 when they failed initial laboratory studies. This was usually an analytical problem rather than a

sampling deficiency. In the major studies which produced the data in the compilation tables, no effort was made to utilize alternate analysis methods. In some cases, potential alternates have been suggested in the Status Table. Method 0010 will collect any organic compound with a boiling point above 100°C. If the compound is not altered by chemical reaction during sampling, field recovery, transport or storage, then identification of a successful quantification scheme becomes a matter of finding effective extraction and determinative analytical methods. The researcher investigating a problem of this nature, should find References 32, 33, 42, 56, 57, and 58 especially helpful.

TABLE 1. SW-846 Proposed Sampling and Analytical Methods for The CAAA of 1990, Title III Hazardous Air Pollutants (HAPs)

CAS No.	Chemical Name	Sampling Method	S. Code (See Footnote 1)	Analysis Method	Comments (See Footnote 2)
75-07-0	Acetaldehyde	0011	f1	8315A	Simultaneous aldehydes possible. Refs. 23, 40
60-35-5	Acetamide	0010	m,sp	8032	May be reactive
75-05-8	Acetonitrile	XACN	f1	8015B 8033	See Refs. 24 & 26.
98-86-2	Acetophenone	0010 0011	f1 f1	3542 8270C 8315A	See References 23 & 40 for 0011.
53-96-3	2-Acetylaminofluorene	0010?	f2f4l1	3542 8270C	
107-02-8	Acrolein	0011? PFBHA	f2, kp l4	8315A GC/MSorECD	Stability problems, even in DNPH See references 45 & 50 for PFBHA approach.
79-06-1	Acrylamide	0010	m, sp	GC/MS or 8316	Polar, water soluble. Poor GC, needs work.
79-10-7	Acrylic Acid	0010 sorbent	m,sp l4	8316 GC/FID	Suspect polymerization may be problem Ref 50&54, prototype needs to be isokinetic.
107-13-1	Acrylonitrile	XACN 0030 0031	s s l8	8015B 8033 5041A 8260B	See Refs. 24 & 26. Purges poorly, needs special attention.
107-05-1	Allyl Chloride	0030 kp 0031 kp 0040	f4 l1 f4 f1	5041A 8260B 5041A 8260B 8260B	0030 recoveries good in lab., 30% from field test (suspect reactivity)
92-67-1	4-Aminobiphenyl	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Ref 50&51.
62-53-3	Aniline	0010? kp acid liquid	f2f4l2 l4	3542 8270C HPLC/PDA	Extraction and reactivity problems. Ref 50&51, prototype needs to be isokinetic.
90-04-0	o-Anisidine	0010 kp acid liquid	f4 l2 s	3542 8270C HPLC/PDA	Ref 50&51, prototype needs to be isokinetic.
1332-21-4	Asbestos	-	-	microscopy	Separate S&A
71-43-2	Benzene	0030 0040	f1 f1	5041A 8260B 8260B	Make sure that the Tenax is clean.
92-87-5	Benzidine	0010? kp acid liquid	f2f4l3 s	3542 8270C HPLC/PDA	May react during sampling. Ref 50&51, prototype needs to be isokinetic.
98-07-7	Benzotrichloride	0010	f2	3542 8270C	
100-44-7	Benzyl Chloride	0010	f1 f2	3542 8270C	
92-52-4	Biphenyl	0010	f1	3542 8270C	
117-81-7	Bis(2-ethylhexyl)phthalate	0010	f2f4l1	3542 8270C	a.k.a. DEHP
542-88-1	Bis(chloromethyl)ether	n, kp 0010	f4 l1	3542 8270C	Reacts quickly with water

		kp 0030	l7		
75-25-2	Bromoform	0010	f1 f2	3542 8270C	
106-99-0	1,3-Butadiene	0040? kp	f4	8260B	Reactive, borderline results.
156-62-7	Calcium cyanamide	0010 M5	s	?	Should be able to collect salt as particulate. Analysis is problematic, low solubility without decomposition.
105-60-2	Caprolactam	0010?	f1f4l1	3542 8270C	Mixed results, suspect hydrolysis.
133-06-2	Captan	0010	m	3542 8270C HPLC	Can be reactive.
63-25-2	Carbaryl	0010?	f1f4l1	3542 8270C	Mixed results.
75-15-0	Carbon Disulfide	0030?	f2f4l2	5041A 8260B	Mixed results.
463-58-1	Carbon Tetrachloride	0030/0031	f1	5041A 8260B	
463-58-1	Carbonyl Sulfide	M15 0040	s	GC/FPD CG/FPD	
120-80-9	Catechol	0010	m	3542 8270C	Careful pH control during extraction mandatory. Recovery may be difficult.
133-90-4	Chloramben	acid liquid	l4	HPLC/PDA	Ref 50&51, prototype needs to be isokinetic
57-74-9	Chlordane	0010	f1	3542 8270C	
7782-50-5	Chlorine	M26/26A 0050 0051	f1	9056 9057	Halogens & halo-acids can be done simultaneously
79-11-8	Chloroacetic Acid	n, sp	n	HPLC	
532-27-4	2-Chloroacetophenone	0010	f1 f2	3542 8270C	
108-90-7	Chlorobenzene	0010 0030? 0031?	f1 f2 f1 f1	3542 8270C 5041A 8260B 5041B 8260B	Above recommended bp limit for 0030/0031, and for 0040.
510-15-6	Chlorobenzilate	0010	f1f3f4	3542 8270C	
67-66-3	Chloroform	0030 0031 0040	f1 f1 s	5041A 8260B 5041A 8260B 8260B	
107-30-2	Chloromethyl Methyl Ether	n kp 0030	l7	5041A 8260B	May decompose during s&a
126-99-8	Chloroprene	0030? 0031	f2f4l1 f1	5041A 8260B 5041A 8260B	Recoveries good in lab., mixed in field. Suspect reactivity.
1319-77-3	Cresols/Cresylic Acid	-	-	-	Determine as individual cresols by methods following.
95-48-7	o-Cresol	0010 NaOH	f1 f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.
108-39-4	m-Cresol	0010 NaOH	f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.

106-44-5	p-Cresol	0010 NaOH	f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.
98-82-8	Cumene	0010	f1	3542 8270C	
94-75-7	2,4-d	0010	s	8151A, 8321A	
3547-04-4	DDE	0010	f1	3542 8270C	CAS #3547-04-4 is on CAAA, The large volume pesticide is 72-55-9. The two are similar (almost congeners) and should behave comparably.
334-88-3	Diazomethane	n, kp	-	-	Very reactive. Derivative method should be developed.
132-64-9	Dibenzofurans	0010	f1	3542 8270C	For PCDF, use Method 0023A or Method 23
84-74-2	1,2-Dibromo-3-Chloro-propane	0010	f1 f4	3542 8270C	
84-74-2	Dibutylphthalate	0010	f1 f4	3542 8270C	Common contaminant
106-46-7	1,4-Dichlorobenzene(p)	0010	f1 f2	3542 8270C	
91-94-1	3,3-Dichlorobenzidene	0010 acid liquid	f4 f5 s	3542 8270C HPLC/PDA	Reactive, no good with 0010. Ref 50&51, prototype needs to be isokinetic.
111-44-4	Dichloroethyl Ether	0010	f1 f2	3542 8270C	Same as bis(2-chloroethyl)ether
542-75-6	1,3-Dichloropropene	0030/0031 0010	f1 f2 f1 f2	5041A 8260B 3542 8270C	Mixed results. May be source sensitive.
62-73-7	Dichlorvos	0010	f1 f2	3542 8270C	
111-42-2	Diethanolamine	n, kp acid liquid	- s	8270 HPLC should	The method of Ref. 50&51 should collect OK if made isokinetic. No benzene ring, so alternate detector may be needed
91-66-7	N,N-Diethyl aniline	0010 acid liquid	f1 f2 s	3542 8270C HPLC/PDA	Compound confused with Dimethylaniline on CAAA, wrong CAS number listed. Ref. 50&51, prototype needs to be isokinetic.
64-67-5	Diethyl Sulfate	n, kp	-	-	Probably special S&A. a.k.a. sulfuric acid, diethyl ester
119-90-4	3-3-Dimethoxybenzidine	kp 0010 acid liquid	f4l3 s	3542 8270C HPLC/PDA	Likely reactive. Ref 50&51, prototype needs to be isokinetic.
60-11-7	Dimethyl Aminoazobenzene	0010? acid liquid	f4 l1 s	3542 8270C HPLC/PDA	Suspect reactivity. Ref 50&51, prototype needs to be isokinetic.
121-69-7	N,N-dimethylaniline	0010 acid liquid	f2 l1 l4	3542 8270C HPLC/PDA	Incorrectly called diethylaniline on CAAA Ref 50&51, prototype needs to be isokinetic
119-93-7	3,3-Dimethyl Benzidine	0010? kp acid liquid	f1f4l3 l4	3542 8270C HPLC/PDA	Mixed results probably due to reactivity. Ref 50&51, prototype needs to be isokinetic
79-44-7	Dimethyl Carbamoyl Chloride	0010	m, sp	8321A	
68-12-2	Dimethyl Formamide	0010	m, sp	8260B, 8141A	
57-14-7	1,1-Dimethyl Hydrazine	0030?	kp l7		Stability problems. Probably needs derivatization method.
131-11-3	Dimethyl Phthalate	0010	f1	3542 8270C	Common contaminant

77-78-1	Dimethyl Sulfate	special	s	special	
534-52-1	4,6-Dinitro-o-Cresol, and salts	0010	f1f2l3	3542 8270C	Bad lab results are puzzling. This test was for the cresol only, not salts.
51-28-5	2,4-Dinitrophenol	0010?	f1f4l3	3542 8270C	Mixed results, very good to very bad.
121-14-2	2,4-Dinitrotoluene	0010	f1	3542 8270C	
123-39-11	1,4-Dioxane	0010 0030	f1 l7	3542 8270C	a.k.a. 1,4-Diethyleneoxide. Easily lost during extraction and concentration. Labeled lab. recovery standard is mandatory.
122-66-7	1,2-Diphenylhydrazine	0010 acid liquid	m s	GC/MS HPLC/PDA	Reactive. Ref 50&51, prototype needs to be isokinetic.
106-89-8	Epichlorohydrin	0010 kp 0030 kp	f2f4l3 l7	3542 8270C	Mostly poor with 0010, worse with 0030. New method needed.
106-88-7	1,2-Epoxybutane	0030	m,sp	5040,(GCMS)	Suspect reactivity problems
140-88-5	Ethyl Acrylate	kp 0030? 0010 sorbent	l8 m,sp l4	 GC/MS GC/FID	Polymerizes easily Ref 50&54.
100-41-4	Ethyl Benzene	0010	f1	3542 8270C	
51-79-6	Ethyl Carbamate	0010?	f1f4l2	3542 8270C	a.k.a. urethane
75-00-3	Ethyl Chloride (Chloroethane)	0030?kp 0031?kp	f2f4l1 f4	5041A 8260B 5041A 8260B	Low bp, 0031 should have done better.
106-93-4	Ethylene Dibromide	0010 0030? 0031?	f1 f2 f1f4l1 f1	3542 8270C 5041A 8260B 5041A 8260B	a.k.a. dibromoethane. Above recommended bp for 0030/0031.
107-06-2	Ethylene Dichloride	0030 0031	f1 f2 f1	5041A 8260B 5041A 8260B	a.k.a. 1,2 dichloroethane
107-21-1	Ethylene Glycol	0010	s	8015B, 8430	
151-56-4	Ethylene Imine (Aziridine)	n kp 0030	l7		Water soluble & polymerizes
75-21-8	Ethylene Oxide	tedlar bag CARB 431	f3	GC/MS GC/FID	Reactivity can cause problems in some matrices
96-45-7	Ethylene Thiourea	0010	m	HPLC/UV 8325	Reactive and water soluble. See Ref. 56 & 57 for HPLC/UV.
75-34-3	1,1 dichloroethane (misnamed Ethylidene Dichloride on CAAA)	0030 0031 0040	f1 f2 f1 f1	5041A 8260B 5041A 8260B 8260B	75-34-3 is really 1,1 dichloroethane. Ethylidene dichloride is 75-35-4
50-00-0	Formaldehyde	0011	f1	8315A	Simultaneous aldehydes possible, ref. 23&40
76-44-8	Heptachlor	0010	f1f4l1	3542 8270C	
118-74-1	Hexachlorobenzene	0010	f1 f2 f4	3542 8270C	Recovery increased greatly with each field test. Last one was 82.6%

87-68-3	Hexachlorobutadiene	0010	f1 f2	3542 8270C	
77-47-4	Hexachlorocyclopentadiene	0010	f2 f4	3542 8270C	Good to mediocre field tests, poor in the lab.
67-72-1	Hexachloroethane	0010	f1	3542 8270C	
822-06-0	Hexamethylene-1,6-diisocyanate	M207-1	f1	M207-2	Reactive, a.k.a. 1,6 diisocyanatohexane a.k.a. HDI
680-31-9	Hexamethylphosphoramide	0010	f4 l3	3542 8270C	Suspect reactivity
110-54-3	Hexane	0030 0040	f1 f1	5041A 8260B 8260B	
302-01-2	Hydrazine	0010	kp	GC/MS	Water soluble & unstable, probably requires special S&A
7647-01-0	Hydrochloric Acid	M26/26A 0050 0051	f1	9056 9057	Halogens & halo-acids can be done simultaneously
7664-39-3	Hydrogen Fluoride	M26/26A	l4	9057	Methods 13A,13B,14 for total fluoride
123-31-9	Hydroquinone	0010	m,sp	GC/MS	Reactive, solubility problems.
78-59-1	Isophorone	0010 0011	f1 f1	3542 8270C 8315A	
58-89-9	Lindane (all isomers)	0010	f1	3542 8270C	a.k.a. hexachlorocyclohexane
108-31-6	Maleic Anhydride	0010	s,kp	HPLC	Reacts with water, must quantitate the acid & report as parent compound
67-56-1	Methanol	0030? M308 MST	m,sp f1 f1	5041A 8260B GC/FID GC/FID	Highly water soluble, may purge poorly See References 59, 60, & 61 for evaluation of M308 and MST.
72-43-5	Methoxychlor	0010	f2	3542 8270C	
74-83-9	Methyl Bromide	0030?kp 0031?kp 0040?kp	f2 f4 f4	5041A 8260B 5041A 8260B 8260B	a.k.a. bromomethane. 0030 barely met f2, 0031 should be better, but was worse. Low bp. 0040 results high.
74-87-3	Methyl Chloride (Chloromethane)	0030 kp 0031 kp 0040	f4 f4 f1	5041A 8260B 5041B 8260B 8260B	Artifact problems with Tenax.
71-55-6	Methyl Chloroform	0030/0031 0040	f1 f1	5041A 8260B 8260B	a.k.a. 1,1,1-trichloroethane
78-93-3	Methyl Ethyl Ketone (2-Butanone)	0011 0030? PFHBA	f4 l8 l4	8315A 5041A 8260B GC/MSorECD	Water solubility causes problems with 5041A purge. See References 45 & 50 for PFBHA approach.
60-34-4	Methyl Hydrazine	0030	kp	5040	Reactive, probably requires special S&A
74-88-4	Methyl iodide	0030/0031	f1	5041A 8260B	a.k.a. Iodomethane
108-10-1	Methyl Isobutyl Ketone (Hexone)	0010 0011	f1 f4	3542 8270C 8315A	See references 45 & 50 for PFBHA approach, 23 & 40 for DNPH (0011).

		PFBHA kp 0030?	I4 I8	GC/MSorECD	
624-83-9	Methyl Isocyanate	M 207-1	f1	M207-2	a.k.a. isocyanic acid, methyl ester, a.k.a. MI. See Ref. 18.
80-61-6	Methyl Methacrylate	0010 kp 0030? sorbent	m,sp I8 I4	5040,(GC/MS) GC/FID	May polymerize Ref 50&54.
1634-04-4	Methyl Tert Butyl Ether	kp 0030?	I8		a.k.a. tert. butyl methyl ether
101-14-4	4,4-Methylene Bis(2-chloroaniline)	0010 acid liquid	m,sp s	GC/MS HPLC/PDA	Suspect reactivity problems during sampling. Ref 50&51, prototype needs to be isokinetic.
75-09-2	Methylene Chloride (dichloromethane)	0030/0031 0040	f1 f1	5041A 8260B 8260B	a.k.a. dichloromethane
101-68-8	Methylene Diphenyl Diisocyanate	M207-1	f1	M207-2	Reactive, See Ref. 18. a.k.a. MDI,a.k.a. 4,4'-Bis(carbonylamino)diphenylmethane.
101-77-9	4,4-Methylenedianiline	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Reactive? Ref 50&51, prototype needs to be isokinetic.
91-20-3	Naphthalene	0010	f1	3542 8270C	
98-95-3	Nitrobenzene	0010	f1	3542 8270C	
92-93-3	4-Nitrobiphenyl	0010	f1	3542 8270C	
100-02-7	4-Nitrophenol	0010	f1f2I3	3542 8270C	Bad lab results are puzzling.
79-46-9	2-Nitropropane	0010,0030	s	GC/MS	
684-93-5	N-Nitroso-N-Methylurea	0010	m,sp	HPLC	Unstable
62-75-9	N-Nitrosodimethylamine	0010	f1	3542 8270C	
59-89-2	N-Nitrosomorpholine	0010	f1	3542 8270C	
56-38-2	Parathion	0010	f1 f2	3542 8270C	
82-68-8	Pentachloronitrobenzene	0010	f1f3f4	GC/MS	
87-86-5	Pentachlorophenol	0010	f1f3f4	3542 8270C	
108-95-2	Phenol	0010 NaOH	f1 f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.
106-50-3	p-Phenylenediamine	0010 acid liquid	m,sp s	GC/MS HPLC/PDA	Reactive, polar, water soluble. Ref 50&51, prototype needs to be isokinetic.
75-44-5	Phosgene	XPHS	I1	GC/MS	Reactive, must be derivatized as collected. See Refs. 52 & 53.
7803-51-2	Phosphine	M29 0060	s	6010 6020 7000	Yields total P value
7723-14-0	Phosphorus	M29 0060	s	6010 6020 7000	Yelds total P value
85-44-9	Phthalic anhydride	0010	s	HPLC	Reacts with water, must quantitate the acid & report as parent compound

		0010 kp	f4 l3	3542 8270C	
1336-36-3	Polychlorinated Biphenyls (Aroclors)	0010 CARB 428	s	3542 GC/MS CARB 428	Combustion destroys Aroclor patterns. Determine isomer groups or individuals.
1120-71-4	1,3-Propane Sultone	0010	m	GC/MS	Polar and reactive.
57-57-8	Beta-Propiolactone	0010	m,sp	GC/MS	May be too reactive
123-38-6	Propionaldehyde	0011	f1	8315A	Simultaneous aldehydes possible. Ref.23&40
114-26-1	Propoxur	0010	f1f2	3542 8270C	a.k.a. Baygon
78-87-5	Propylene Dichloride	0030 0031	f1 f2 f1	5041A 8260B 5041A 8260B	a.k.a. 1,2 dichloropropane
75-56-9	Propylene Oxide	kp 0030 0040	l7 m, sp		Reactive, water soluble, a.k.a. 1,2 propylene oxide
75-55-8	1,2-Propylenimine	n kp 0030	l7		May be reactive
91-25-5	Quinoline	0010 acid liquid	f1 l4	3542 8270C HPLC/PDA	Ref 50&51, prototype needs to be isokinetic
106-51-4	Quinone	0010 0011?	f4l3kp f2,kp	3542 8270C 8315A	May be reactive,a.k.a. 1,4-benzoquinone,a.k.a. p-benzoquinone
100-42-5	Styrene	0010?	f1f4l1	3542 8270C	Low f4 results puzzling. Reactivity?
96-09-3	Styrene Oxide	0010 kp	f4 l3	3542 8270C	Reactive. A.k.a. 1,2 epoxyethylbenzene
1746-01-6	2,3,7,8-Tetrachlorodibenzo -p-Dioxin	M23 0023A	f1	M23 8290	Special care needed during recovery and analysis.
79-34-5	1,1,2,2-Tetrachloroethane	0010	f1	3542 8270C	
127-18-4	Tetrachloroethylene	0010 0030/0031	f2 f1 f2	3542 8270C 5041A 8260B	a.k.a. tetrachloroethene,.a.k.a perchloroethylene
7550-45-0	Titanium Tetrachloride	M29 0060	s	6010 6020 7000	For total titanium
108-88-3	Toluene	0010 0030 0040	fi f2 f1 f1	3542 8270C 5041A 8260B 8260B	
95-80-7	2,4-Toluene Diamine	0010 acid liquid	m,sp l4	GC/MS HPLC/PDA	Reactive Ref 50&51, prototype needs to be isokinetic.
584-84-9	2,4-Toluene Diisocyanate	M207-1	f1	M207-2	Reacts with water,a.k.a. TDI
95-53-4	o-Toluidine	0010? acid liquid	f2f4l1 l4	3542 8270C HPLC/PDA	Mixed results, may be reactive. Ref 50&51, prototype needs to be isokinetic.
8001-35-2	Toxaphene (Chlorinated Camphene)	0010	s	GC/MS,8250	
120-82-1	1,2,4-Trichlorobenzene	0010	f1 f2	3542 8270C	
79-00-5	1,1,2-Trichloroethane	0010 0030/0031	f1 f2 f1	3542 8270C 5041A 8260B	

		0040	f1	8260B	
79-01-6	Trichloroethylene	0030/0031	f1	5041A 8260B	a.k.a. trichloroethene
95-95-4	2,4,5-Trichlorophenol	0010	f1	3542 8270C	
88-06-2	2,4,6-Trichlorophenol	0010	f1 f2	3542 8270C	
121-44-8	Triethylamine	n kp 0030 acid liquid	l7 s	HPLC should	a.k.a. N,N-diethylethanimine. Suspect reactivity. The method of Ref. 50&51 should collect OK. No benzene ring, so alternate detector may be needed
1582-09-8	Trifluralin	0010 acid liquid	f4l2kp m, kp	3542 8270C HPLC/PDA	Suspect reactivity; a.k.a. Treflan Ref 50&51, prototype needs to be isokinetic. Analysis method needs modification.
540-84-1	2,2,4-Trimethylpentane	0030 0040	f2 f1	5041A 8260B 8260B	a.k.a. isooctane
108-05-4	Vinyl Acetate	kp 0030? sorbent	l8 l4	 GC/FID	 Ref 50&54.
593-60-2	Vinyl Bromide	0030?kp 0031?kp 0040 M106	f2f4l1 f4 f1	5041A 8260B 5041A 8260B 8260B GC/MS	
75-01-4	Vinyl Chloride	0030 kp 0031? kp 0040 M106	f1f4l1 f4 l1 f1 l5	5041A 8260B 5041A 8260B 8260B GC/MS	Mixed results, 0030 is questionable. Poor field results for 0031 are puzzling, may be due to reactivity.
75-35-4	Vinylidene Chloride	0030/0031 0040 M106	f1/f1 f1 l5	5041A 8260B 8260B GC/MS	a.k.a. 1,1 dichloroethene. a.k.a. 1,1 dichloroethylene
1330-20-7	Xylenes(mixture)	0010	f1	3542 8270C	Determine individual xylenes, not total.
95-47-6	o-Xylene	0010	f1	3542 8270C	
108-38-3	m-Xylene	0010	f1	3542 8270C	
106-42-3	p-Xylene	0010	f1	3542 8270C	
-	Antimony Compounds	M29 0060	f1	6010 6020 7000	
-	Arsenic Compounds	M29 0060	f1	6010 6020 7000	Also Method 108 & 108A
-	Beryllium Compounds	M29 0060	f1	6010 6020 7000	Also Method 103 & 104
-	Cadmium Compounds	M29 0060	f1	6010 6020 7000	
-	Chromium Compounds	M29 0060	f1	6010 6020 7000	M29 or 0060 for total chromium, 0061 for hexavalent Cr.
-	Cobalt Compounds	M29 0060	s	6010 6020 7000	

-	Coke Oven Emissions	Method 109	-	-	
-	Cyanide Compounds	XHCN	I1	XHCN	XHCN for HCN, CARB426 for total cyanide.
-	Glycol Ethers	n 0010	- s	- 8430, 8015B	Category too general, however a method is possible for individual compounds. Should be isokinetic, probably 0010.
-	Lead Compounds	M29 0060	f1	6010 6020 7000	Also Method 12
-	Manganese Compounds	M29 0060	f1	6010 6020 7000	
-	Mercury Compounds	M29 0060	f1	7470	Also Methods 101,101A,102. For speciation research see references 50 & 55.
-	Mineral Fibers				
-	Nickel Compounds	M29 0060	f1	6010 6020 7000	
-	Polycyclic Organic Matter	0010 CARB 429	f3	3542 8270C CARB 429	Individual compounds are determined, not total POM, more or less synonymous with pna, pah, pac.
-	Radionuclides (including radon)	M111 M114 M115			
-	Selenium Compounds	M29 0060	f1	6010 7000	

[1] STATUS AND RECOVERY TABLE CODE DEFINITIONS

R %Recovery of spiked standard.
C Method 301 bias correction factor
An underlined method is not recommended for the listed air toxic.
? Effectiveness of the method for the listed air toxic is questionable or showed mixed results.
f1 Data are available from at least one Method 301 field test where 143% R 76.9% (equivalent to 0.70 C 1.30) and the RSD of R was 50%.

f2 Data are available from at least one Method 301 field test where 150% R 50% (equivalent to 0.67 C 2.00) and the RSD of R was 50%.
f3 Data are available from at least one field test not fully qualifying as Method 301 where 150% R 50% (equivalent to 0.67 C 2.00) and the RSD of R was 50%. Some of the recovery data may be better than the minimum shown, and the test may only have failed to meet minimum replicate criteria for full Method 301 statistical analysis.
f4 Data are available from at least one Method 301 field test where R 50% or R 150% or the RSD of R was 50%.
f5 Data are available from at least one field test not fully qualifying as Method 301 where R 50% or R 150% or the RSD of R was 50%.
I1 Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. The RSD of R was 50%, and 143% R 76.9% (equivalent to 0.70 C 1.30). This is essentially a successful Method 301 test in the laboratory.
I2 Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. The RSD of R was 50%, and 150% R 50% (equivalent to 0.67 C 2.00).
I3 Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. R 50% or R 150% or the RSD of R was 50% or unknown.
I4 Other laboratory test data are available, where 143% R 76.9% (equivalent to 0.70 C 1.30) and the RSD of R 50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.
I5 Other laboratory test data are available, where 150% R 50% (equivalent to 0.67 C 2.00) and the RSD of R 50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.
I6 Other laboratory test data are available, where R 50% or R 150% or the RSD of R was 50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.

I7	Laboratory tests showed no response in VOST analytical system (5041A & 8260B). See References 5, 7, 11, and 16.
I8	Laboratory tests showed weak response in VOST analytical system (5041A & 8260B). See References 5, 7, 11, and 16. Special attention or modification necessary for reliable operation.
s	Should work. For sampling methods, no confirmatory field or laboratory data has been identified, but the structure of the compound or its similarity to validated compounds makes the prognosis optimistic.
m	Might work. This designation usually implies that the technique given should work if the compound survives the sampling and analysis process, but that we have strong reservations about its ability to do so. This status is usually linked with reactivity/instability. Many compounds are stable enough to analyze, but will not tolerate prolonged exposure to water, NO_2, or other materials during sampling.
n	No known adequate method. This always means we know of no reliable method for this pollutant. We usually have identified a number of unreliable methods for the pollutant. If negative data are available, the sampling method will be underlined.
sp	Suspected problems. The suspected problem is given in the comments, and is often related to reactivity.
kp	Known problems. This is similar to the suspected problem except that our fears have been confirmed by data. If data indicate questionable or inconsistent performance, the sampling method will be followed by a question mark.

[2]SELECTED AIR TOXICS METHODS REFERENCES

1. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Field Evaluation of EPA Method 0040 (Volatiles Using Bags), EPA-600/R-98/030, PB98-133085, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1998.
2. McGaughey, J.F., Bursey, J.T., Merrill, R.,G., Fuerst, R.G. and Jackson, M.D., "Field Evaluation of EPA Proposed Method 0040 (Sampling and Analysis of Volatile Compounds Using Tedlar Bags)," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 159-165.
3. Johnson, L.D.,"Research and Evaluation of Organic Hazardous Air Pollutant Source Emission Test Methods," J. Air & Waste Manage. Assoc., 46, pp.1135-1148, December 1996.
4. Margeson, J.H., Knoll, J.E., Midgett, M.R., Wagoner, D.E., Rice, J., and Homolya, J.B.,"An Evaluation of The Semi-VOST Method for Determining Emissions from Hazardous Waste Incinerators,"J. Air Pollut. Control Assoc., 37:(9)1067 (1987).
5. Jackson, M.D., Knoll, J.E., Midgett, M.R., Bursey, J.T., McAllister R.A., Merrill, R.G, "Evaluation of VOST and SemiVOST Methods for Halogenated Compounds in the Clean Air Act Amendments Title III, Bench and Laboratory Studies," Proceedings of the National A&WMA Meeting, Kansas City, June 1992, Air & Waste Management Association, Pittsburgh, PA, 1992.
6. Jackson, M.D., Knoll, J.E., Midgett, M.R., Bursey, J.T., McGaughey, J.F., Merrill, R.G. "Evaluation of VOST and Semi-VOST Methods for Halogenated Compounds in the Clean Air Act Amendments Title III, Validation Study at Fossil Fuel Plant," Proceedings of the National A&WMA Meeting, Denver, CO, June 1993, Air & Waste Management Association, Pittsburgh, PA, 1993.
7. Bursey, J.T., Merrill, R.G., McAllister, R.A., McGaughey, J.F., Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List, Volumes 1 & 2, EPA-600/R-93/123a, EPA-600/R-93/123b, PB93-227163, PB93-227171, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1993.
8. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Field Test of a Generic Method for Halogenated Hydrocarbons, EPA-600/R-93/101, PB93-212181AS, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1993.
9. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Jackson, M.D.,"Field Test of a Generic Method for The Sampling and Analysis of Halogenated Hydrocarbons Listed in Title III of The Clean Air Act Amendments of 1990," Proceedings of the 13th Annual International Incineration Conference, Houston, TX, May 1994, University of California, Irvine, CA, 1994.
10. Jackson, M.D., Bursey, J.T., McGaughey, J.F., Merrill, R.G.," An Evaluation of the SemiVOST Method for Halogenated Compounds at a Chemical Manufacturing Facility," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1995, VIP-50, Air & Waste Management Association, Pittsburgh, PA, 1995, pp 227-232.
11. Jackson, M.D., Bursey, J.T., McGaughey, J.F., Merrill, R.G.,"Application of VOST and SemiVOST to Nonhalogenated CAAA Compounds," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1995, VIP-50, Air & Waste Management Association, Pittsburgh, PA, 1995, pp 233-238.

12. Jackson, M.D., Johnson, L.D., McGaughey, J.F., Wagoner, D.E., Bursey, J.T., Merrill, R.G., "Improvements in Preparation of Samples Generated by SW-846 Method 0010," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1994, VIP-39, Air & Waste Management Association, Pittsburgh, PA, 1994, pp 331-338.
13. Jackson, M.D., Bursey, J.T.,McGaughey, J.F. and Merrill, R. G., "An Evaluation of the SemiVOST Method for non-Halogenated Compounds at a Agricultural Chemical Manufacturing Facility", Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 134-141.
14. Bursey, J.T.,McGaughey, J.F. and Merrill, R. G., Field Evaluation at an Agricultural Manufacturing Facility of VOST and SemiVOST Methods for Selected CAAA Organic Compounds, EPA/600-R-97/037, PB97-174585, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1997.
15. Jackson, M.D.,McGaughey, J.F., Merrill, R. G., and Bursey, J.T., "Method Evaluation Study: The Application of Semi-VOST to the Nonhalogenated Semivolatile Organic Compounds from the Clean Air Act Amendments", Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996, VIP-64, Air & Waste Management Association, Pittsburgh, PA, 1996 pp 620-625.
16. Bursey, J.T.,McGaughey, J.F. and Merrill, R. G., Field Evaluation (First) of VOST and Semi-VOST Methods for Selected CAAA Organic Compounds at a Coal Fired Plant, EPA/600-R-97/076, PB97-196117, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1997.
17. Bursey, J.T., McGaughey, J.F. and Merrill, R. G., Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST at an Agricultural Chemical Manufacturing Facility, EPA/600-R-97/033, PB97-162499, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1997.
18. McGaughey, J.F., Foster, S.C., Merrill, R.G., Laboratory Development and Field Evaluation of A Generic Method for Sampling and Analysis of Isocyanates, EPA-600/R-95/144, PB95-273801, U.S. Environmental Protection Agency,Research Triangle Park, NC, August 1995.
19. Jackson, M.D.; Johnson, L.D.; McGaughey, J.F.; Wagoner, D.E.; Bursey, J.T.; Merrill, R.G., "Improvements in Preparation of Samples Generated by SW-846 Method 0010," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1994, VIP-39, Air & Waste Management Association, Pittsburgh, PA, 1994, pp 331-338.
20. Johnson, L.D., Fuerst, R.G., Foster, A.L. and Bursey, J.T.,"Replacement of Charcoal Sorbent In The Sampling of Volatile Organics from Stationary Sources," Intern. J. Environ. Anal. Chem.,Vol 62, pp. 231-244, (1996).
21. Eaton, W.C.; Jaffe, L.B.; Rickman, E.E.; Jayanty, R.K.M., Field Tests of Chloroform Collection/Analysis Methods, EPA-600/R-94/082, PB94-176948, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1994.
22. Eaton, W.C.; Jaffe, L.B.; Rickman, E.E.; Jayanty, R.K.M.; Wilshire, F.W.; Knoll, J.E., "Validation of a Test Method for Collection and Analysis of Chloroform Emissions from Stationary Sources," J. Air & Waste Manage. Assoc., 46, pp 66-71, 1996.
23. Steger, J.L., Knoll, J.E., "Dynamic Spiking Studies Using the DNPH Sampling Train," presented at EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.
24. Steger, J.L., Bursey, J.T., and Epperson, D., Acetonitrile Field Test, EPA-600/R-97/140, PB98-133143, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1997.
25. R.G. Fuerst, T.J. Logan, M.R. Midgett and J. Prohaska, "Validation Studies of the Protocol for the Volatile Organic Sampling Train," J. Air Pollut. Control Assoc., 37:(4)388 (1987).
26. Johnson, L.D., Fuerst, R.G., Steger, J.L., and Bursey, J.T., "Evaluation of a Sampling Method for Acetonitrile Emissions from Stationary Sources," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 149-158.
27. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Jackson, M.D., Johnson, L.D., Fuerst, R.G., "Comparison of a Modified VOST Sampling Method with SW-846 Method 0030 at a Chemical Manufacturing Facility," Proceedings of the 13th Annual International Incineration Conference, Houston, TX, May 1994, University of California, Irvine, CA, 1994.
28. Jackson, M.D., Johnson, L.D., Fuerst, R.G., McGaughey, J.F., Bursey, J.T., Merrill, R.G., "Field Evaluation of a Modified VOST Sampling Method," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1994, VIP-39, Air & Waste Management Association, Pittsburgh, PA, 1994, pp 354-360.

29. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method, EPA-600/R-94/130, PB95-142055, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1994.
30. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST Test at a Chemical Manufacturing Facility, EPA-600/R-96/133, PB97-115349, U.S. Environmental Protection Agency, Research Triangle Park, NC, November 1996.
31. McGaughey, J.F., Bursey, J.T., Merrill, R.G., Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility, EPA-600/R-94/113, PB95-129144, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1994.
32. Rice, J., McGaughey, J.F., Bursey, J.T., Merrill, R.G., Harvan, D., Handbook of GC/MS Data and Information for Selected Clean Air Act Amendments Compounds, EPA-600/R-94/021, PB94-155884, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1994.
33. Wagoner, D.E., Merrill, R.G., McGaughey, J.F., Bursey, J.T., Evaluation of CAAA Compounds: Approaches for Stationary Source Method Development, EPA-600/R-96/091, PB96-193206, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1996.
34. Jackson, M.D.,McGaughey, J.F., Merrill, R. G., and Bursey, J.T., "Method Evaluation Study: The Application of VOST to the Nonhalogenated Volatile Organic Compounds from the Clean Air Act Amendments", Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996, VIP-64, Air & Waste Management Association, Pittsburgh, PA, 1996 pp 613-619.
35. Jackson, M.D., Bursey, J.T.,McGaughey, J.F. and Merrill, R. G., "An Evaluation of the VOST Method for non-Halogenated Compounds at a Agricultural Chemical Manufacturing Facility", Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 129-133.
36. Prohaska, J., T.J. Logan, R.G. Fuerst, M.R. Midgett, Validation of the Volatile Organic Sampling Train (VOST) Protocol, Volume 1, Laboratory Validation Phase, PB86-145547, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1986.
37. Prohaska, J., T.J. Logan, R.G. Fuerst, M.R. Midgett, Validation of the Volatile Organic Sampling Train (VOST) Protocol, Volume 2, Field Validation Phase, PB86-145554, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1986.
38. Wilshire, F.W., Knoll, J.E., Foster, S.C. and McGaughey, J.F., "Development and Validation of a Source Test Method for 2,4-Toluene Diisocyanate," in Proceedings of the 1993 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-34, Air & Waste Management Association, Pittsburgh, PA, 1993, pp 399-407.
39. Wilshire, F.W., Knoll, J.E., Foster, S.C. and McGaughey, J.F., "Field Test and Validation of a Source Test Method for Methylene Diphenyl Diisocyanate," Proceedings of the 87th Annual National A&WMA Meeting, Cincinnati, OH, June 1994, Air & Waste Management Association, Pittsburgh, PA, 1994.
40. Steger, J.L. and Workman, G.S., Field Validation of the DNPH Method for Aldehydes and Ketones, EPA/600/R96/050, PB96-168398, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 1996.
41. Jackson, M.D., Johnson, L.D., "Sampling and Analysis Information Aids for Stationary Source Personnel," Proceedings of the EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1994, VIP-39, Air & Waste Management Association, Pittsburgh, PA, 1994, pp 315-318.
42. Jackson, M.D., Johnson, L.D., Stationary Source Sampling and Analysis Directory, Version 2.1, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1995, EPA/600/R-97/028, PB98-120033 (Report/Manual) and PB-500598 (Database on floppy disk) February 1997.
43. Steger, J.L., Merrill, R.G., Parrish, C.R., and Johnson, L.D., Development and Evaluation of a Source Sampling and Analysis Method for Hydrogen Cyanide, EPA/600/R-98/xxx, PB98-xxxxxx, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1998.
44. Steger, J.L., Merrill, R.G., Fuerst, R.G., Johnson, L.D., Jackson, M.D. and Parrish, C.R., "Development and Evaluation of a Source Sampling and Analysis Method for Hydrogen Cyanide," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 114-122.
45. Fan, Z., Peterson, M.R., Jayanty, R.K.M., "Development of a Test Method for Carbonyl Compounds from Stationary Source Emissions," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 92-97.

46. Bursey, J.T., McGaughey, J.F., Merrill, R. G., Knoll, J.E., Ward, T.E., and Jackson, M.D., "Field Testing to Complete Validation of a Manual Method for High Levels of Phenolic Compounds," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 142-149.
47. Pau, J.C., Romeu, A.A., Whitacre, M., and Coates, J.T., Validation of Emission Sampling and Analysis Test Method for PCDDs and PCDFs II, EPA-600/R3-90/047, PB90-235847/AS, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1990.
48. Cooke, M., DeRoos, F., Rising, B., Jackson, M.D., Johnson, L.D., and Merrill, R.G., "Dioxin Collection from Hot Stack Gas Using Source Assessment Sampling System and Modified Method 5 Trains - An Evaluation," presented at Ninth Annual Research Symposium on Land Disposal, Incineration, and Treatment of Hazardous Waste, Ft. Mitchell, KY, May 1983.
49. Fan, Z., Peterson, M.R., Jayanty, R.K.M., Wilshire, F.W., "Measurement of Carbonyl Compounds from Stationary Source Emissions by a PFBHA-ECD Method," presented at the 91st Annual National Meeting of the Air & Waste Management Association, San Diego, CA, June 1998.
50. Peterson, M.R., Fan, Z., Jaffe, L.B., Albritton, J.R., Grohse, P.M., Jayanty, R.K.M., Research, Development, and Evaluation of Stationary Source Emission Test Methods for Air Toxics,Letter Report, Research Triangle Institute to U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1998.
51. Peterson, M.R., Pate, B.A., Wright, R.S.,Jayanty, R.K.M., Wilshire, F.W., "A Test Method for the Measurement of Arylamines in Stationary Source Emissions," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996, VIP-64, Air & Waste Management Association, Pittsburgh, PA, 1996 pp 577-582.
52. Steger, J.L., Coppedge, E.A. and Johnson, L.D., "Research and Development of A Source Method for Phosgene," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996, VIP-64, Air & Waste Management Association, Pittsburgh, PA, 1996, pp 285-289.
53. Steger, J.L., Bursey, J.T., Merrill, R.G., and Epperson, D., Research and Development of a Field-Ready Protocol for Sampling of Phosgene from Stationary Source Emissions: Diethylamine Reagent Studies, EPA/600/R-98/xxx, PB98-xxxxxx, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1998.
54. Peterson, M.R., Jaffe, L.B., Jayanty, R.K.M., Wilshire, F.W., "A Test Method for the Measurement of Acrylics in Stationary Source Emissions," presented at the 90th Annual National Meeting of the Air & Waste Management Association, Toronto, Ontario, Canada, June 1997.
55. Giglio, J.J., O'Rourke, J.J., Grohse, P.M., Wilshire, F.W., Ryan, J., Linak, W., The Development of a Method for the Speciation of Source Mercury Emissions," Presented at the International Conference on Incineration and Thermal Treatment Technologies, Salt Lake City, UT, May, 1998.
56. James, R.H., Adams, R.E., Finkel, J.M., Miller, H.C., and Johnson, L.D., "Evaluation of Analytical Methods for the Determination of POHC in Combustion Products," J. Air Pollution Control Association, 35, 959 (1985).
57. James, R.H., Adams, R.E., Finkel, J.M., Miller, H.C., POHC Analysis Methods for Hazardous Waste Incineration, Vol. 1,Parts 1 & 2, Vol. 2, EPA/600/8-87-037 a, b & c, PB87-227286/AS, PB87-227294/AS, PB87-227302/AS, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1987.
58. James, R.H., Adams, R.E., Farr, L.B., Miller, H.C., PIC Analysis Methods, EPA-600/9-87-011, PB87-208955/AS, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1987.
59. Pate, B.A., Peterson, M.R., Rickman, E.E., Jayanty, R.K.M., Test Method for the Measurement of Methanol Emissions from Stationary Sources, EPA-600/R-94/080, PB94-170297, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1994.
60. Pate, B.A., Peterson, M.R., Jayanty, R.K.M., Wilshire, F.W., Knoll, J.E., "Development of a Test Method for the Measurement of Gaseous Methanol Emissions from Stationary Sources," in Proceedings of the 1993 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, VIP-34, Air & Waste Management Association, Pittsburgh, PA, 1993, pp 393-398.
61. Peterson, M.R.,Pate, B.A., Rickman, E.E., Jayanty, R.K.M., Wilshire, F.W., "Validation of a Test Method for the Measurement of Methanol Emissions from Stationary Sources," J. Air & Waste Manage. Assoc., 45, pp. 3-11, 1995.
62. Eaton, W.C., Jaffe, L.B., Rickman, E.E., Jayanty, R.K.M., Field Tests of Chloroform Collection/Analysis Methods, EPA-600/R-94/082, PB94-176948, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1994.

63. Eaton, W.C., Jaffe, L.B., Rickman, E.E., Jayanty, R.K.M., Wilshire, F.W., Knoll, J.E., "Validation of a Test Method for Collection and Analysis of Chloroform Emissions from Stationary Sources," J. Air & Waste Manage. Assoc., 46, pp 66-71, 1996.
64. Bursey, J.T., McGaughey, J.F., Steger, J.L., Merrill, R. G., Field Testing to Complete Validation of a Manual Method for High Levels of Phenolic Compounds, Draft Final Report, U.S. Environmental Protection Agency, Research Triangle Park, NC.
65. U.S. EPA Tentative Method 317, Phenol, Manual Method, U.S. Environmental Protection Agency, Research Triangle Park, NC.