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AP42 Section 5.1

Related: 2

Title: AB 2588 Pooled Source Emission Test Program
Vol. 3 Compilation of Test Methods
Series of tests conducted on 19 refinery sources

July 1990

Almega Corporation

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THE ALMEGA CORPORATION

AB2588 POOLED SOURCE EMISSION
TEST PROGRAM

THE ALMEGA CORPORATION PROJECT I6551
THE ALMEGA CORPORATION REPORT I6551-4

VOLUME III
Compilation of Test Methods

PREPARED FOR

Western States Petroleum Association
505 N. Brand Boulevard, Suite 1400
Glendale, California 91203

THE ALMEGA CORPORATION

PLEASE REPLY TO:

WEST COAST

July 26, 1990

Western States Petroleum Association
505 N. Brand Boulevard, Suite 1400
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Attention: Mr. Robert Stockdale, Chairman
AB2588 Working Group

Subject: AB 2588 Pooled Source Emission Test Program
The Almega Corporation Project I6551
The Almega Corporation Report I6551-4
Volume III- Compilation of Test Methods

Gentlemen:

INTRODUCTION

A series of tests were conducted on 19 refinery sources to develop preliminary emission factors to aid refiners in preparation of the 1989 emission estimate report mandated by AB2588, Air Toxics "Hot Spots" Information and Assessment Act of 1987. Testing was performed on a representative number of heaters, boilers and cogeration gas fired turbines, and one sulfur recovery unit, one gasoline loading rack and one asphalt recovery incinerator.

This volume contains reference copies of the CARB test methods and the USEPA multiple metal train test method used throughout this program. Details of modifications of these methods for compounds for which test methods do not exist have been included in Volume I of this report.

Respectfully submitted,
THE ALMEGA CORPORATION

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APPENDIX A

CARB Method 1

Sample and Velocity Traverse for Stationary Sources

State of California
Air Resources Board

Method 1

Sample and Velocity Traverses for Stationary Sources

Adopted: June 29, 1983
Amended: March 28, 1986

METHOD 1 - SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES

1. Principle and Applicability

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

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

The requirements of this method must be considered before construction of a new facility from which emissions will be measured; failure to do so may require subsequent alterations to the stack or deviation from the standard procedure. Cases

involving variants are subject to approval by the Control Agency's authorized representative.

2. Procedure

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

2.2 Determining the Number of Traverse Points

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

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

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

TABLE 1-1. Cross-sectional Layout for Rectangular Stacks

Number of Traverse Points	Matrix layout
9	3 x 3
12	4 x 3
16	4 x 4
20	5 x 4
25	5 x 5
30	6 x 5
36	6 x 6
42	7 x 6
49	7 x 7

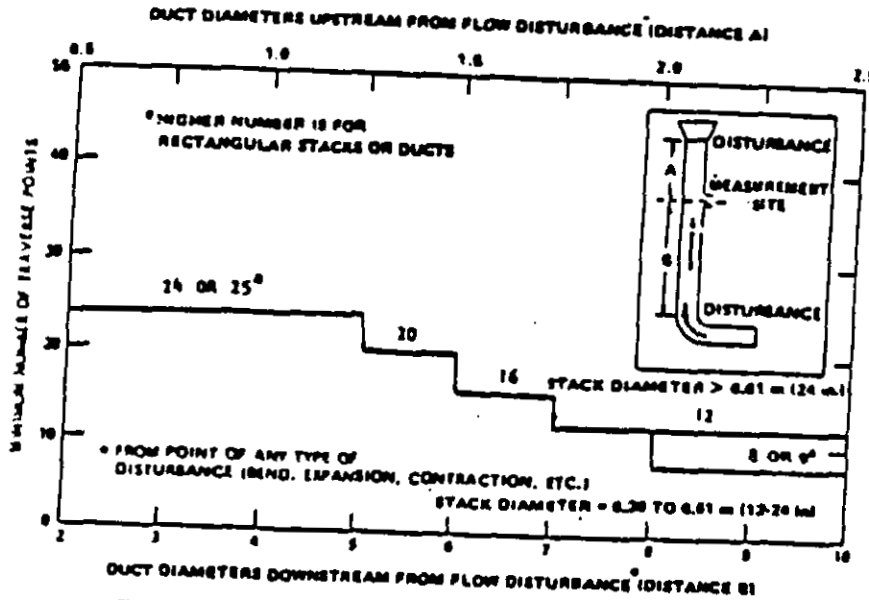

Figure 1-1. Minimum number of traverse points for particulate traverses.

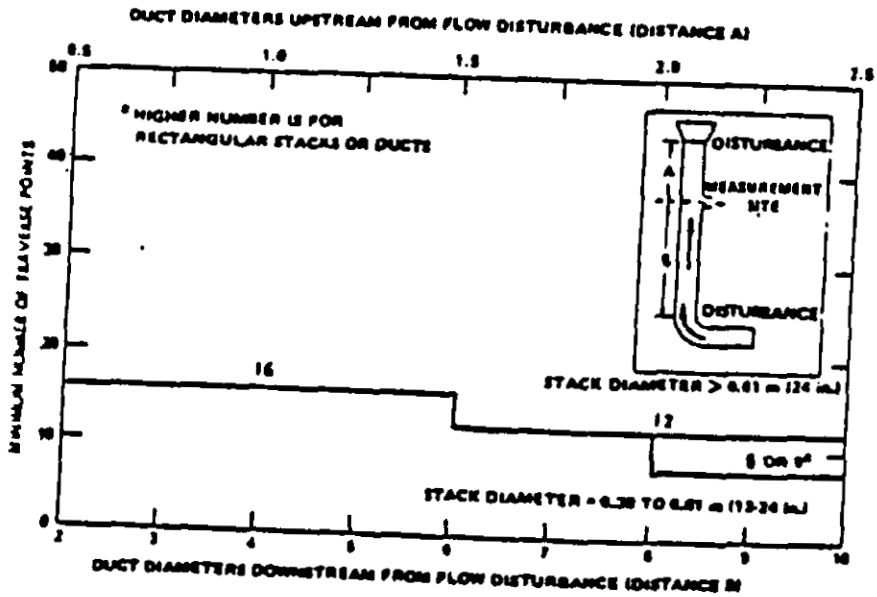

Figure 1-2. Minimum number of traverse points for velocity (nonparticulate) traverses.

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

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

2.3 Cross-Sectional Layout and Location of Traverse Points

2.3.1 Circular Stacks. Locate the traverse points on two perpendicular diameters according to Table 1-2 and the example shown in Figure 1-3. Any equation that gives the same values as those in Table 1-2 may be used in lieu of Table 1-2. For particulate traverses, one of the diameters must be in a plane containing the greatest expected concentration variation, e.g., after bends, one diameter shall be in the plane of the bend. This requirement becomes less critical as the distance from the disturbance increases; therefore, other diameter locations may be used, subject to approval of the Control Agency's authorized representative.

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

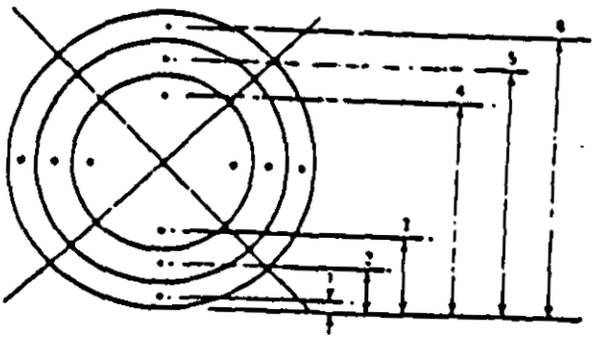

Figure 1-3. Example showing circular stack cross section divided into 12 equal areas, with location of traverse points indicated.

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

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

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	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	3.8	3.3	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	18.9	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	29.8	25.0	21.9	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.3	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	38.2	32.3
12						97.9	89.1	83.1	76.4	69.4	60.7	38.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.3	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									96.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										95.1	91.3	86.6
20										96.7	94.0	89.5
21											96.5	92.1
22											98.8	94.5
23												96.8
24												98.8

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

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

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

2.3.1.2 Stacks with Diameters Equal to or Less Than 0.61 m (24 in.). Follow the procedure in Section 2.3.1, noting only that any "adjusted" points should be relocated away from the stack walls to: (1) a distance of 1.3 cm (0.50 in.); or (2) a distance equal to the nozzle inside diameter, whichever is larger.

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

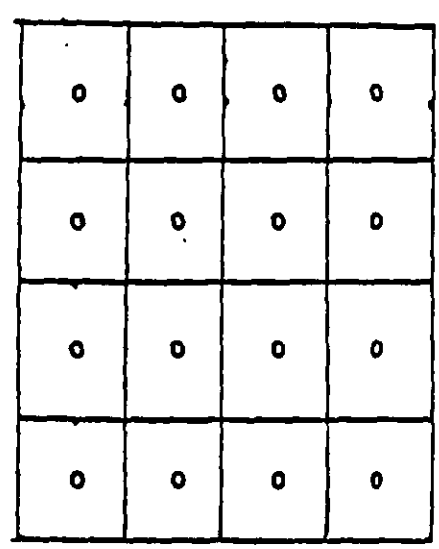

Figure 1-4
Example Showing Rectangular Stack Cross Section Divided into Twelve Equal Areas, with a Traverse Point at Centroid of Each Area

If the tester desires to use more than the minimum number of traverse points, expand the "minimum number of traverse points" matrix (see Table 1-1) by adding the extra traverse points along one or the other or both legs of the matrix; the final matrix need not be balanced. For example, if a 4 x 3 "minimum number of points" matrix were expanded to 36 points, the final matrix could be 9 x 4 or 12 x 3, and would not necessarily have to be 6 x 6. After constructing the final matrix, divide the stack cross-section into as many equal rectangular, elemental areas as traverse points, and locate a traverse point at the centroid of each equal area.

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

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

2.4 Verification of Absence of Cyclonic Flow. In most stationary sources, the direction of stack gas flow is essentially parallel to the stack walls. However, cyclonic flow may exist (1) after such devices as cyclones and inertial demisters following venturi

scrubbers, or (2) in stacks having tangential inlets or other duct configurations which tend to induce swirling; in these instances, the presence or absence of cyclonic flow at the sampling location must be determined. The following techniques are acceptable for this determination.

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

3. Bibliography

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

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

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

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

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

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

APPENDIX B

CARB Method 2

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

State of California
Air Resources Board

Method 2

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

Adopted: June 29, 1983

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

1. Principle and Applicability

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

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

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

2. Apparatus

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Control Agency's Authorized Representative) to be capable of meeting the specifications will be considered acceptable.

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

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

A standard pitot tube may be used instead of a Type S, provided that it meets the specifications of Sections 2.7 and 4.2; note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas

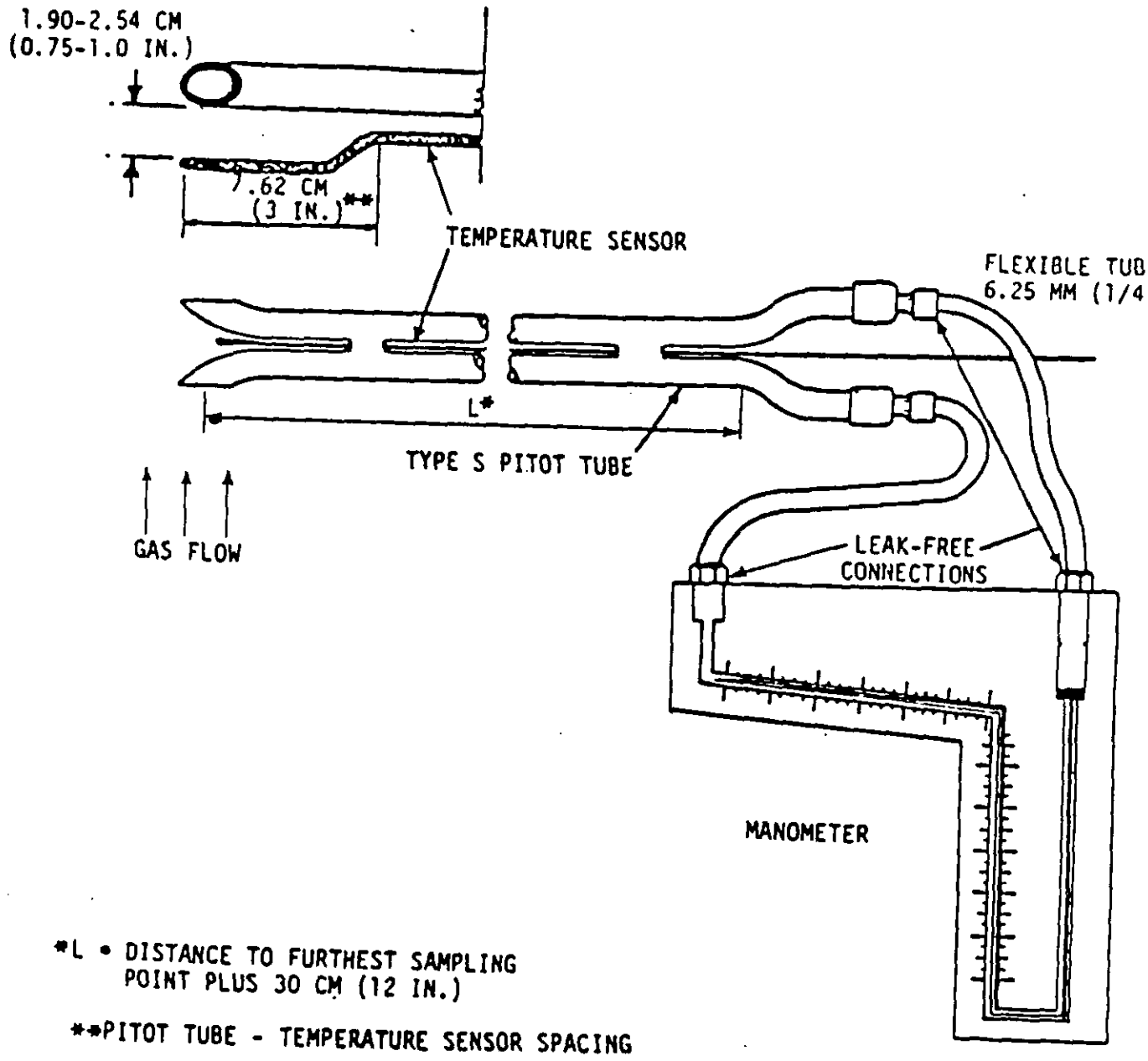

Figure 2.1 Type S pitot tube-manometer assembly.

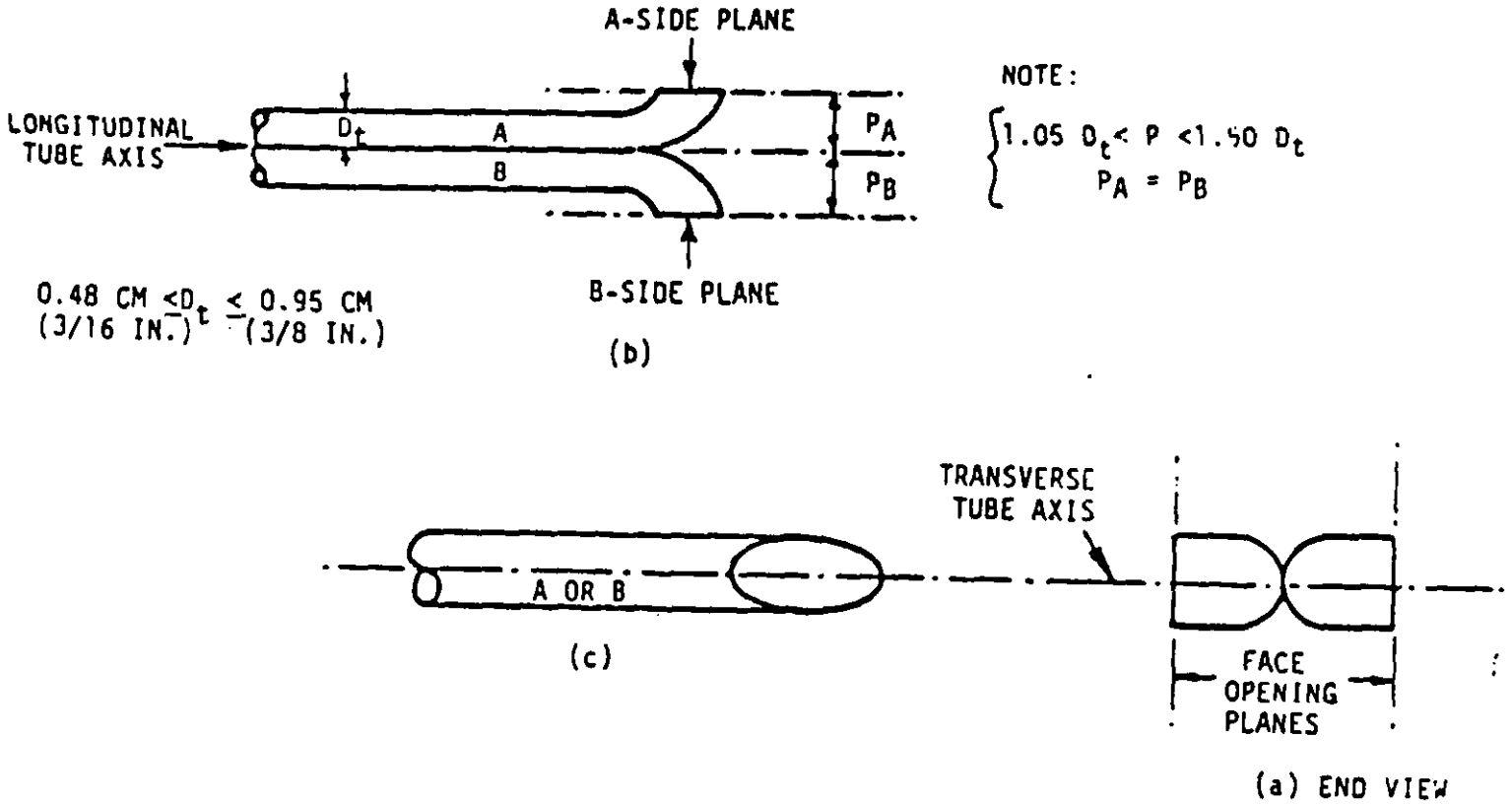

Figure 2.2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

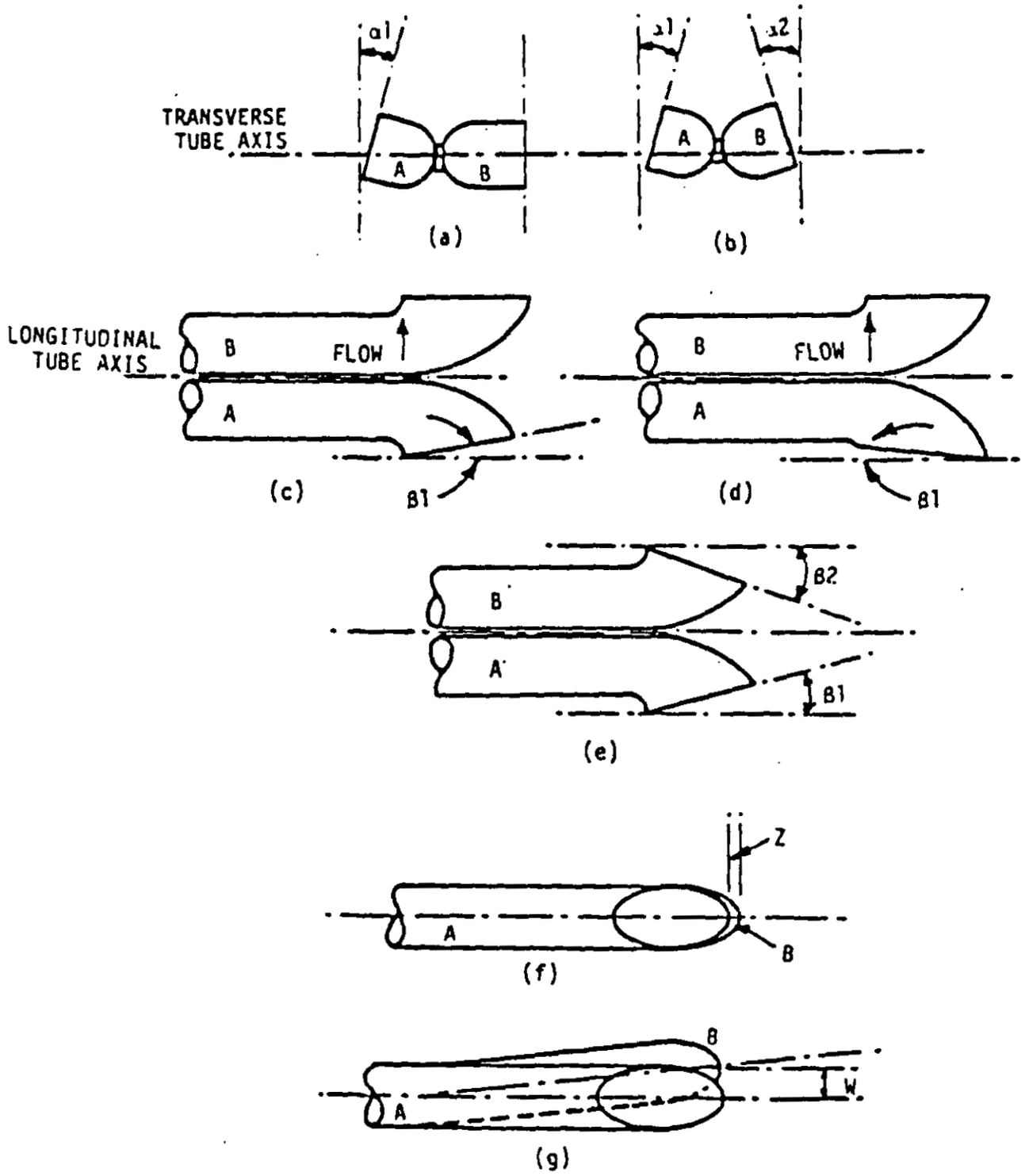

Figure 2.3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect Cp so long as α_1 and α_2 <10°, β_2 <5°, z <0.32 cm (1/8 in.) and w<0.08 cm (1/32 in.).

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

2.2 Differential Pressure Gauge. An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10-in. (water column) inclined-vertical manometer, having 0.01-in. H_2O divisions on the 0- to 1-in. inclined scale, and 0.1-in. H_2O divisions on the 1- to 10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H_2O. However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Control Agency's Authorized Representative), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than

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

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

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

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

n = Total number of traverse points.

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

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

Note: If differential pressure gauges other than inclined manometers are used (e.g., magnehelic gauges), their calibration must be checked after each test series. To check the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three

points, approximately representing the range of Δp values in the stack. If, at each point, the values of Δp as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured Δp values and final results shall be used, subject to the approval of the Control Agency's Authorized Representative.

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

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

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

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

2.7 Calibration Pitot Tube. When calibration of the Type S pitot tube is necessary (see Section 4), a standard pitot tube is used

as a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Bureau of Standards, Route 270, Quince Orchard Road, Gaithersburg, Maryland, or (2) by calibration against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criterion given in 2.7.1 through 2.7.5 below and illustrated in Figure 2.4 (see also Citations 7, 8, and 17 in Section 6) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 $\pm$0.01.

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

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

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

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

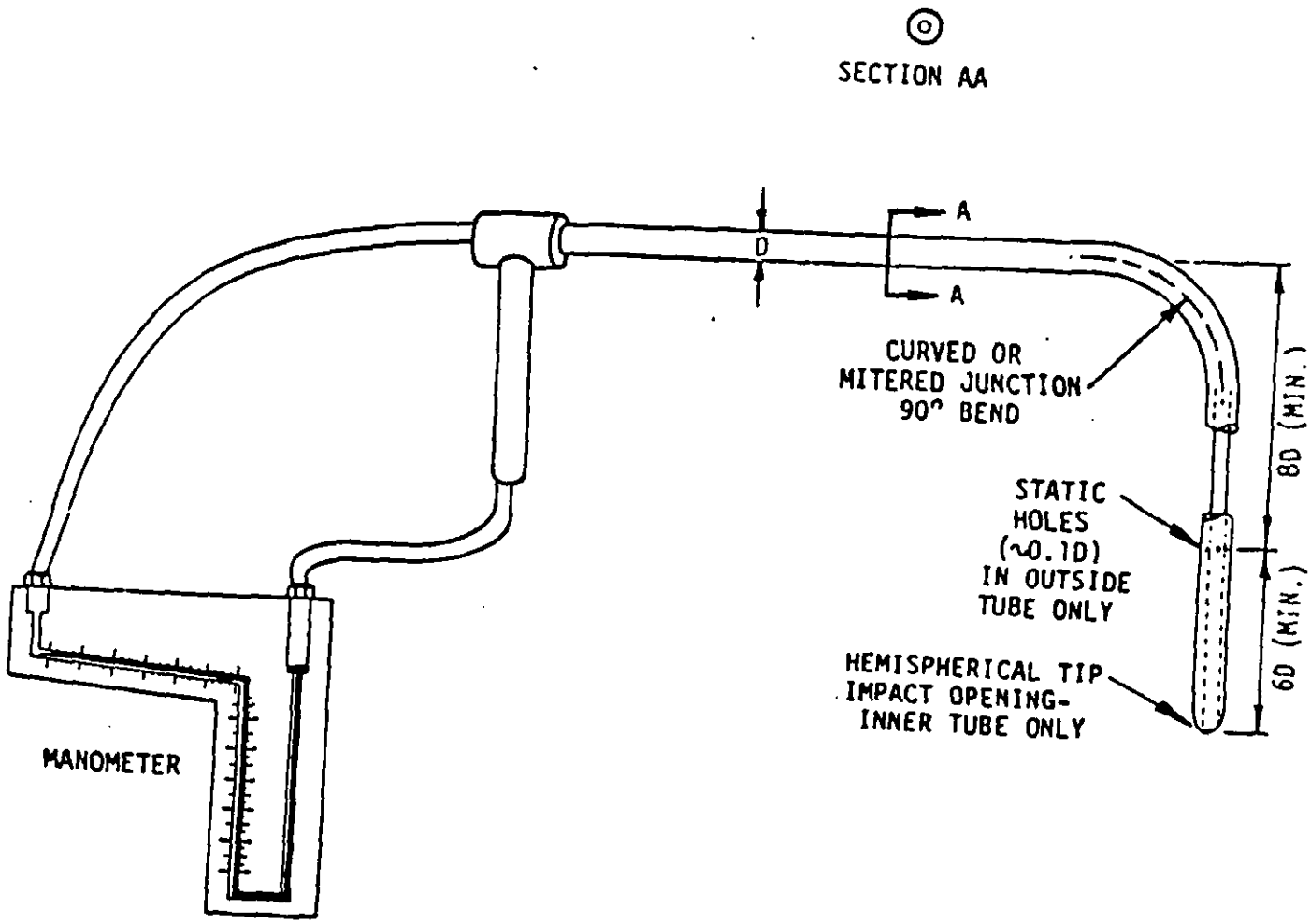

Figure 2.4 Standard pitot tube design specifications.

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2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type S Pitot Tube Calibration

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

3. Procedure

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

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

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

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

3.5 Determine the atmospheric pressure.

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

FIGURE 2.5

State of California
AIR RESOURCES BOARD

File No. _____

Stationary Source Division
Engineering Evaluation Branch

VELOCITY TRAVERSE DATA

Traverse Point Number	Distance From inside wall, in.		Velocity Head in. H_2O	Stack Temperature (T_s), °F	$\sqrt{\Delta P}$
	Without Offset	With Offset			
Average					

Plant _____

Pitot Tube Factor --------

Sampling Site _____

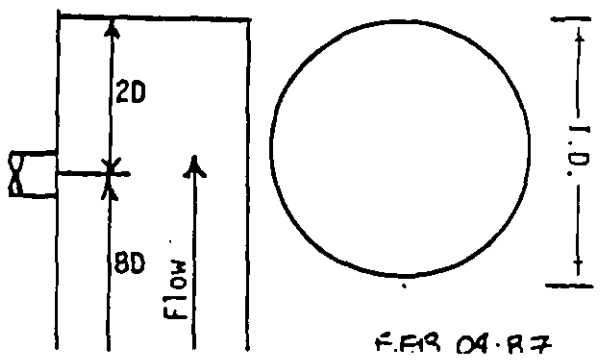
Barometric Pressure, in. Hg _____

Static Pressure in Stack (Pg) in. Hg _____

Remarks _____

_____

Operators _____ Date _____



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

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

4. Calibration

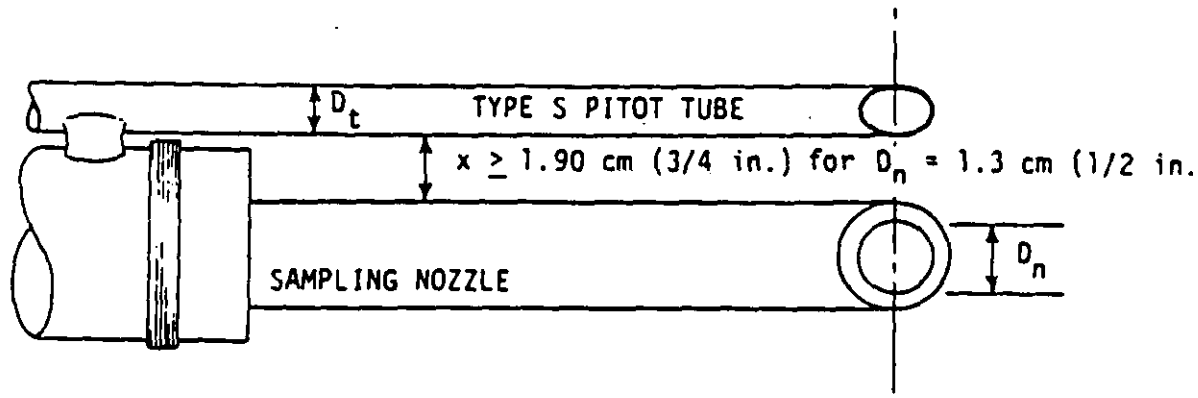
4.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube in top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figure 2-2 or 2-3. The pitot tube shall not be used if it fails to meet these alignment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

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

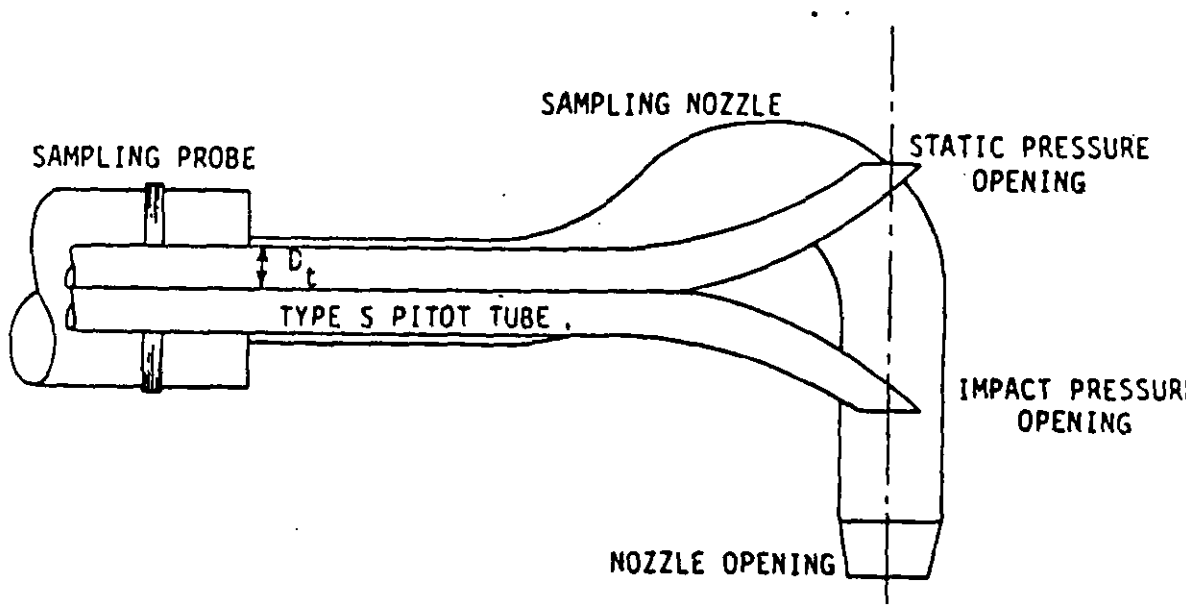
If D_t, P_A, and P_B are outside the specified limits, the pitot tube must be calibrated as outlined in 4.1.2 through 4.1.5 below.

4.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Citation 9 in Section 6); therefore, an assigned (or otherwise known) baseline coefficient value may or may not be valid for a given assembly.

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



(a) BOTTOM VIEW: SHOWING MINIMUM PITOT-NOZZLE SEPARATION.



(b) SIDE VIEW: TO PREVENT PITOT TUBE FROM INTERFERING WITH GAS FLOW STREAMLINES APPROACHING THE NOZZLE, THE IMPACT PRESSURE OPENING PLANE OF THE PITOT TUBE SHALL BE EVEN WITH OR DOWNSTREAM FROM THE NOZZLE ENTRY PLANE

Figure 2.6. Required pitot tube-sampling nozzle configuration to prevent aerodynamic interference; buttonhook-type nozzle; centers of nozzle and pitot opening aligned; in respect to flow direction, D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

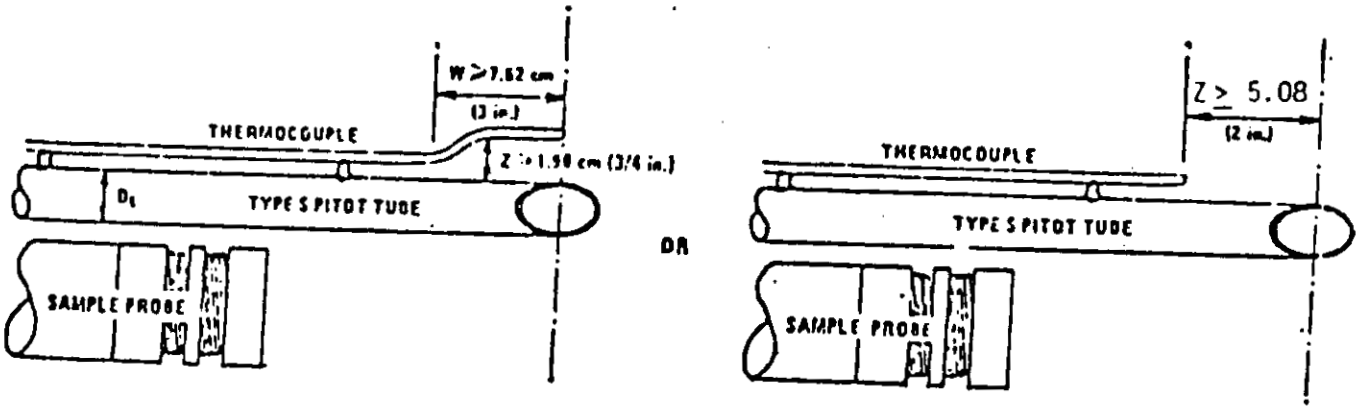


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

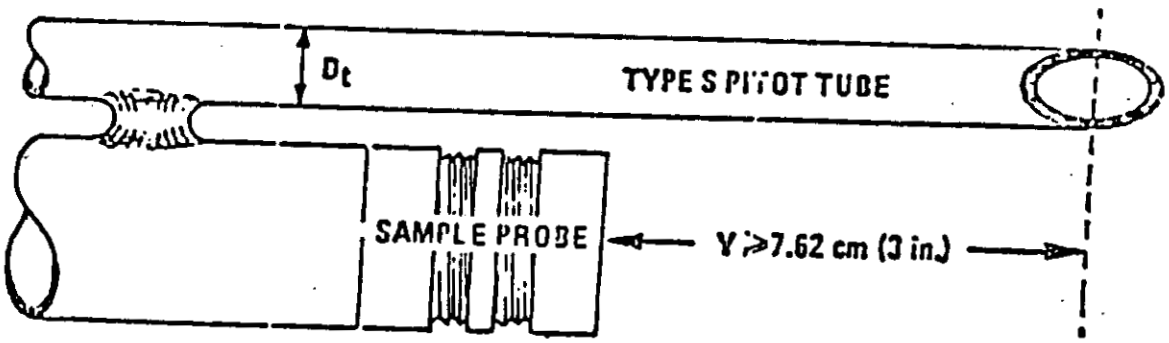


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

values of the intercomponent spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

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

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

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

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

following equation, to determine the number of duct diameters:

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

Equation 2-1

where: D_e = Equivalent diameter

L = Length

W = Width

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

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

4.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 915 m/min (3,000 ft/min). This velocity must be constant with time to guarantee steady flow during

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

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

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

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

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

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

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

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

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

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

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

PITOT TUBE IDENTIFICATION NUMBER: _____ DATE: _____

CALIBRATED BY: _____

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

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

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

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

Figure 2-9. Pitot tube calibration data.

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4.1.3.9 Perform calculations, as described in Section 4.1.4 below.

4.1.4 Calculations

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

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

Equation 2-2

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

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

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

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

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

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

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

Equation 2-3

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

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

Equation 2-4

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

4.1.5 Special Considerations

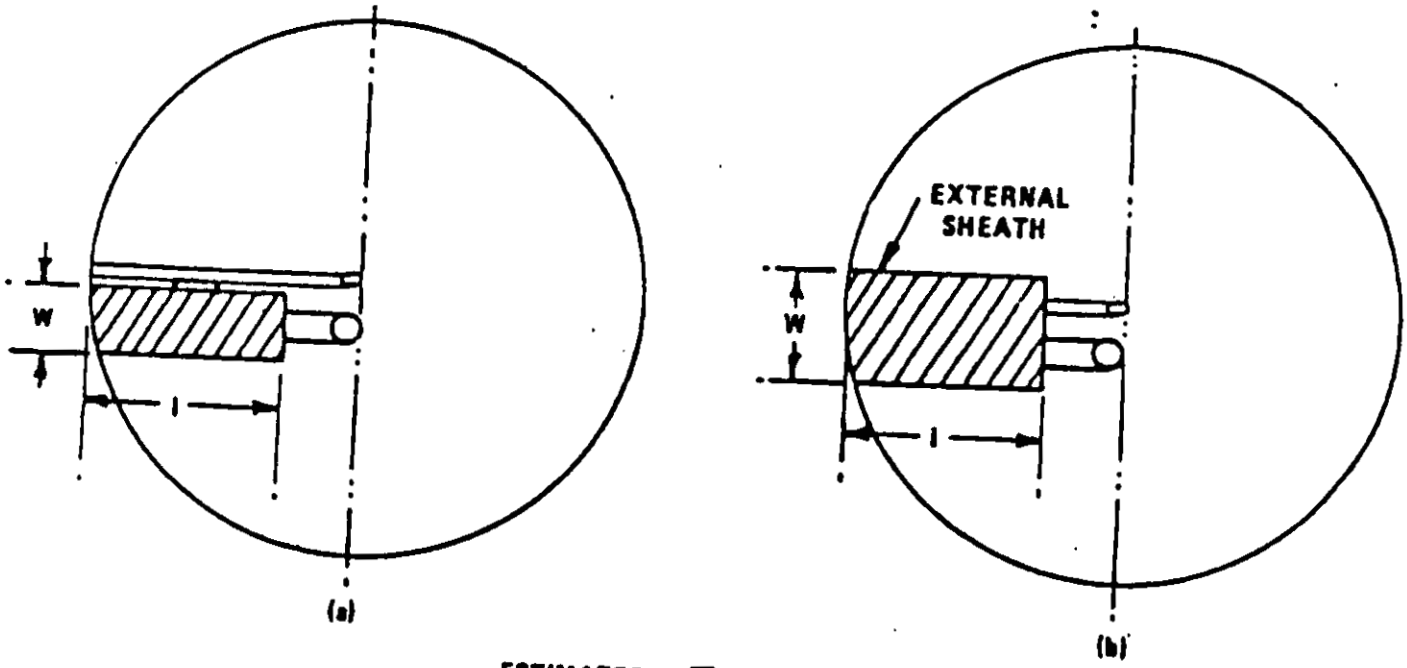
4.1.5.1 Selection of Calibration Point

4.1.5.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The Type S pitot coefficients so obtained, i.e., $\bar{C}_p$ (side A) and $\bar{C}_p$ (side B), will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components

(nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2-6 through 2-8).

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

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



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

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

4.1.5.2 For those probe assemblies in which pitot tube nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specification illustrated in Figure 2-6a), the value of $C_{p(s)}$ depends upon the amount of free-space between the tube and nozzle, and therefore is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or 1/4 in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min. (3,000 ft/min.), which is the calibration velocity; note also that it is not necessary to draw an isokinetic sample during calibration. (Citation 9 in Section 6.)

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

4.1.6 Field Use and Recalibration

4.1.6.1 Field Use

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

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

4.1.6.2 Recalibration

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

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

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

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

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

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

the test results shall be made, subject to the approval of the Control Agency's Authorized Representative.

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

5. Calculations

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

5.1 Nomenclature

A = Cross-sectional area of stack, m^2 (ft^2).

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

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant.

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

for the metric system and

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

for the English system.

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

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

$= M_d (1-Bws) + 18.0\ Bws$

Equation 2-5

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

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

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

$= P_{bar} + P_g$

Equation 2-6

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

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

t_s = Stack temperature °C (°F).

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

$= 273 + t_s$ for metric

Equation 2-7

$= 460 + t_s$ for English

Equation 2-8

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

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

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

3,600 = Conversion factor, sec/hr.

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

5.2 Average stack gas velocity

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

Equation 2-9

5.3 Average stack gas dry volumetric flow rate

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

Equation 2-10

6. Bibliography

1. Mark, L.S. Mechanical Engineer's Handbook. New York, McGraw-Hill Book Co., Inc. 1951.

2. Perry, J.H. Chemical Engineers' Handbook. New York. McGraw-Hill Book Co., Inc. 1960.

3. Shigehara, R.T., W. F. Todd, and W.S. Smith. Significance of Errors in Stack Sampling Measurements. U.S. Environmental Protection Agency, Research Triangle Park, NC. (Presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, MO June 14-19, 1970.)

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

5. Vennard, J.K. Elementary Fluid Mechanics. New York. John Wiley and Sons, Inc. 1947.

6. Fluid Meters - Their Theory and Application. Amercian Society of Mechanical Engineers, New York, NY. 1959.

7. ASH RAE Handbook of Fundamentals. 1972. p. 208.

8. Annual Book of ASTM Standards, Part 26. 1974. p. 648.

9. Vollaro, R.F. Guidelines for Type S Pitot Tube Calibration. U.S. Environmental Protection Agency. Research Triangle Park, NC. (Presented at 1st Annual Meeting, Source Evaluation Society, Dayton, Ohio, September 18, 1975.)

10. Vollaro, R.F. A Type S Pitot Tube Calibration Study. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. July 1974.

11. Vollaro, R.F. The Effects of Impact Opening Misalignment on the Value of the Type S Pitot Tube Coefficient. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

12. Vollaro, R.F. Establishment of a Baseline Coefficient Value for Properly Constructed Type S Pitot Tubes. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

13. Vollaro, R.F. An Evaluation of Single-Velocity Calibration Technique as a Means of Determining Type S Pitot Tube Coefficients. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. August 1975.

14. Vollaro, R.F. The Use of Type S Pitot Tubes for the Measurement of Low Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

15. Smith, Marvin L. Velocity Calibration of EPA Type Source Sampling Probe. United Technologies Corporation, Pratt and Whitney Aircraft Division, East Hartford, CT. 1975.

16. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. November 1976.

17. Ower, E. and R.C. Pankhurst. The Measurement of Air Flow, 4th Ed. London, Pergamon Press. 1966.

18. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. Novmeber 1976. (Unpublished Paper)

19. Gnyp, A.W., C.C. St. Pierre, D.S. Smith, D. Mozzon, and J. Steiner. An Experimental Investigation of the Effect of Pitot Tube-Sampling Probe Configurations on the Magnitude of the S Type Pitot Tube Coefficient for Commercially Available Source Sampling Probes. Prepared by the University of Windsor for the Ministry of the Environment, Toronto, Canada. February 1975.

APPENDIX C

CARB Method 3

Gas Analysis for Carbon Dioxid, Oxygen, Excess Air and Dry Molecular Weight

State of California
Air Resources Board

Method 3

Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight

Adopted: June 29, 1983
Amended: March 28, 1986

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

1. Principle and Applicability

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

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

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

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

2. Apparatus

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

2.1 Grab Sampling (Figure 3-1)

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

plug of glass wool is satisfactory for this purpose). Any other material inert to O_2, CO_2, CO, and N_2 and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

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

2.2 Integrated Sampling (Figure 3.2)

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

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

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

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

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

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

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

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

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

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

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

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

3. Dry Molecular Weight Determination

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

3.1 Single-Point, Grab Sampling and Analytical Procedure

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

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

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

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

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

3.2 Single-Point, Integrated Sampling and Analytical Procedure

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

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

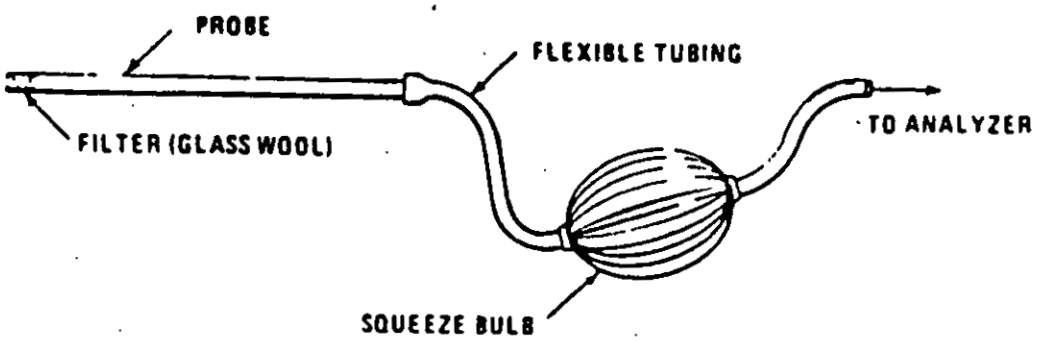


Figure 3.1 Grab sampling train.

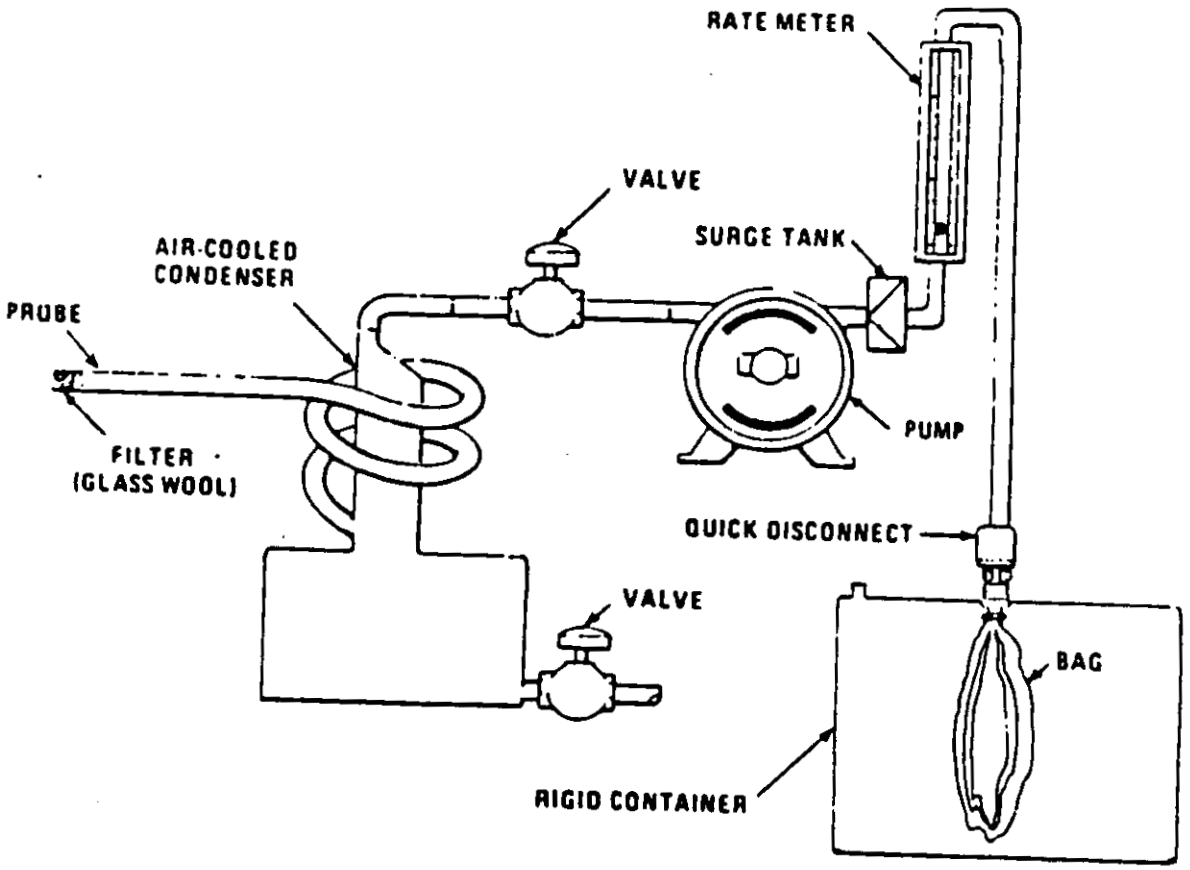


Figure 3.2 Integrated gas sampling train.

FIGURE 3-3—SAMPLING RATE DATA

Time	Traverse pt.	Q (cfm)	% dev.*
Average			

* % dev. = $\left(\frac{Q - Q_{avg}}{Q_{avg}}\right) 100\%$

must be less than 10%

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

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

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

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

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

3.3 Multi-Point, Integrated Sampling and Analytical Procedure

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

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

4. Emission Rate Correction Factor or Excess Air Determination

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

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

4.1 Single Point, Grab Sampling and Analytical Procedure

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

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

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

percent; and (3) calculate percent excess air as outlined in Section 6.2.

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

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. Note: Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure

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

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

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

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

the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2 and percent CO from 100 percent; (3) calculate percent excess air, as outlined in Section 6.2.

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

4.2.6 Repeat the analysis until the following criteria are met:

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

4.2.6.2 For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less

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

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

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

4.3 Multi-Point, Integrated Sampling and Analytical Procedure

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

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

4.4 Quality Control Procedures.

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

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

concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F_o check minimally useful.

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

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 3.3}$$

Where:

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

$\%CO_2$ = Percent CO_2 by volume (Dry Basis).

20.9 = Percent O_2 by volume in ambient air.

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

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

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

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

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

$$F_o = \frac{0.209\ F_d}{F_c} \qquad \text{Eq. 3-4}$$

Fuel Type	F_o range
Coal:	
Anthracite and Lignite	1.018-1.130
Bituminous	1.083-1.230
Oil	
Distillate	1.260-1.413
Residual	1.270-1.370
Gas	
Natural	1.600-1.838
Propane	1.434-1.586
Butane	1.405 1.553
Wood	1.000 1.120
Wood Bark	1.003-1.130

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

5. Leak-Check Procedure for Orsat Analyzers

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

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

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

5.1.3 Record the meniscus position.

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

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

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

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

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

6. Calculations

6.1 Nomenclature.

M_d	=	Dry molecular weight, g/g-mole (lb/lb-mole)
Percent EA	=	Percent excess air.
Percent CO_2	=	Percent CO_2 by volume (dry basis).
Percent O_2	=	Percent O_2 by volume (dry basis).
Percent CO	=	Percent CO by volume (dry basis).
Percent N_2	=	Percent N_2 by volume (dry basis).
0.264	=	Ratio of O_2 to N_2 in air, v/v.
0.280	=	Molecular weight of N_2 or CO, divided by 100.
0.320	=	Molecular weight of O_2 divided by 100.
0.440	=	Molecular weight of CO_2 divided by 100

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

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

Equation 3-1

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

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

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

Equation 3-2

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

7. Bibliography

1. Altshuller, A.P. Storage of Gases and Vapors in Plastic Bags. International Journal of Air and Water Pollution. 6:75-81. 1963.

2. Conner, William D. and J.S. Nader. Air Sampling with Plastic Bags. Journal of the American Industrial Hygiene Association. 25:291-297. 1964.

3. Burrell Manual for Gas Analysis, Seventh edition. Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, PA 15219. 1951.

4. Mitchell, W.J. and M.R. Midgett. Field Reliability of the Orsat Analyzer. Journal of Air Pollution Control Association 26:491-495. May 1976.

5. Shigehara, R.T., R.M. Neulicht, and W.S. Smith. Validating Orsat Analysis Data from Fossil Fuel-Fired Units. Stack Sampling News 4(2):24-26. August 1976.

APPENDIX D

CARB Method 4

Determination of Moisture Content in Stack Gas

State of California
Air Resources Board

Method 4

Determination of Moisture Content in Stack Gases

Adopted: June 29, 1983

METHOD 4 - DETERMINATION OF MOISTURE CONTENT IN STACK GASES

1. Principle and Applicability

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

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

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

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic,

pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon results of the approximation method, unless the approximation method is shown, to the satisfaction of the Control Agency's Authorized Representative, to be capable of yielding results within 1 percent H_2O of the reference method.

Note - The reference method may yield questionable results when applied to saturated gas streams or to streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to $\pm$ 1°C (2°F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) using a psychrometric chart and making appropriate

corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods, subject to the approval of the Control Agency's Authorized Representative, shall be used.

2. Reference Method

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

2.1 Apparatus

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

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

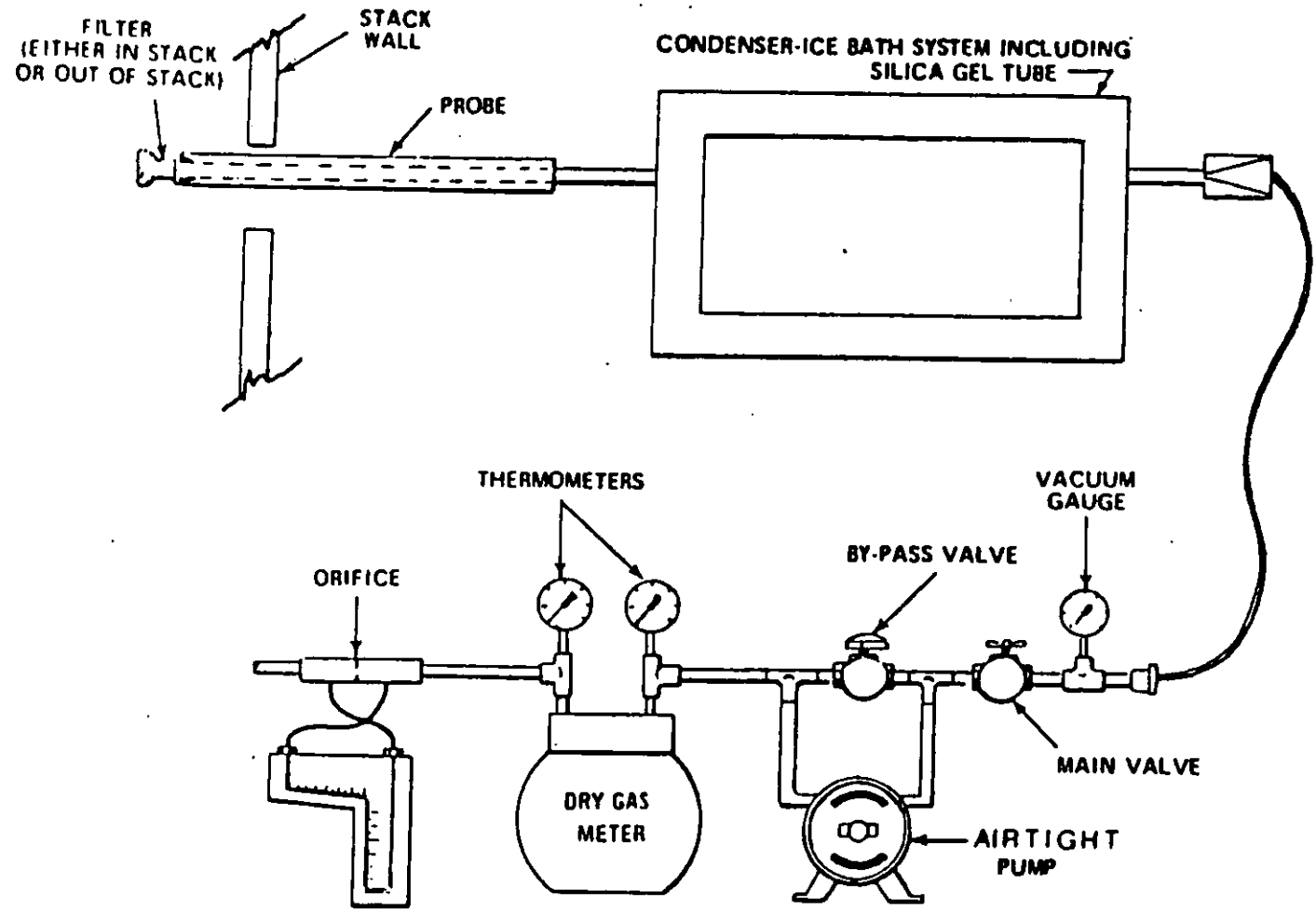


Figure 4.1 Moisture sampling train (Reference Method).

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

2.1.2 Condenser. The condenser consists of four impingers connected in series with ground glass, leak-free fittings or any similarly leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 centimeter (1/2 inch) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Control Agency's Authorized Representative.

The first two impingers shall contain known volumes of water, the third shall be empty, and the fourth shall contain a known weight of 6 to 16 mesh indicating type silica gel, or equivalent desiccant. If the silica gel has been previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. 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 Control Agency's Authorized Representative) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water, either gravimetrically or volumetrically, and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures, or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap, with exit gases kept below 20°C (68°F), and determining the weight gain.

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

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

2.1.4 Metering System. This system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring

volume to within 2 percent, and related equipment as shown in Figure 4-1. Other metering systems, capable of maintaining a constant sampling rate and determining sample gas volume, may be used, subject to the approval of the Control Agency's Authorized Representative.

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

2.1.6 Graduated Cylinder and/or Balance. These items are used to measure condensed water and moisture caught in the silica gel to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

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

and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 Unless otherwise specified by the Control Agency's Authorized Representative, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in), and a minimum of twelve traverse points shall be used in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Control Agency's Authorized Representative. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Place known volumes of water in the first two impingers. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

2.2.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no

greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

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

2.2.4 During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Control Agency's Authorized Representative. For each run, record the

FIGURE 4.2

Project No. _____
Date _____
Time _____

WATER VAPOR CALCULATIONS

Standard Conditions 68°F and 29.92 in. Hg

Ambient Conditions ___°F and _____ in. Hg

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

Assume 1 gram H_2O = 1 ml H_2O

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

$P_{ma} = P_{bar} + (\Delta H/13.6) = (\quad\quad) + \frac{(____)}{13.6} =$ _____ in. Hg

$V_{m_{std}} = \frac{528\ ^oR}{29.92\ in.\ Hg} \frac{V_m P_{ma}}{T_m} = (17.64)(_____)(_____) =$ _____ S DCF

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

$V_{w_{std}} = (0.04707\ \frac{ft^3}{ml})(V_{1c}) = (0.04707)(\quad\quad) =$ _____ SCF

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

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

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

% OF H_2O AT SATURATION

Temp. °F	% H_2O	Temp. °F	% H_2O	Temp. °F	% H_2O
50	1.2	130	15.1	180	51.1
60	1.7	140	19.7	185	57.0
70	2.5	150	25.3	190	63.6
80	3.5	155	28.7	195	70.8
90	4.8	160	32.3	200	78.6
100	6.5	165	36.4	205	87.0
110	8.7	170	40.8	210	96.2
120	11.5	175	45.7	212	100.0

data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

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

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

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

2.3.1 Nomenclature.

B_{ws}	=	Proportion of water vapor, by volume, in the gas stream.
M_w	=	Molecular weight of water, 18.0 g/g mole (18.0 lb/lb-mole).
P_m	=	Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in Hg).
P_{std}	=	Standard absolute pressure, 760 mm Hg (29.92 in Hg)
R	=	Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g-mole) (K^o) for metric units and 21.85 (in Hg) (ft^3)/(lb-mole) (^oR) for English units.
T_m	=	Absolute temperature at meter. ^oK (^oR).
T_{std}	=	Standard absolute temperature, 293° K (528°R).
V_m	=	Dry gas volume measured by the dry gas meter, dcm (dcf).
ΔV_m	=	Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).
$V_m(std)$	=	Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc}(std)$	=	Volume of water vapor condensed corrected to standard conditions, scm (scf).
$V_{wsg}(std)$	=	Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).
V_f	=	Final volume of condenser water, ml.
V_i	=	Initial volume, if any, of condenser water, ml.
W_f	=	Final weight of silica gel plus impinger, g.

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

Y = Dry gas meter calibration factor.

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

2.3.2 Volume of water vapor condensed.

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

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

Equation 4-1

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

= 0.04707 ft^3/ml for English units

2.3.3 Volume of water vapor collected in silica gel.

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

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

Equation 4-2

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

= 0.04715 ft^3/g for English units

2.3.4 Sample gas volume.

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

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

Equation 4-3

where: K_3 = 0.3858 °K/mm Hg for metric units

17.65 °R/in. Hg for English units

NOTE: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of V_m in Equation 4-3 as described in Section 6.3 of Method 5.

2.3.5 Moisture Content

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

Equation 4-4

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

2.3.6 Verification of constant sampling rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3. Approximation Method

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

3.1 Apparatus

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

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

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

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

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

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

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

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

3.1.9 Graduated cylinder, 25 ml.

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

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

3.2 Procedure

3.2.1 Place exactly 5 ml distilled water in each impinger. Leak-check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in

Hg). Note the time rate of change of the dry gas meter dial; alternatively, a rotameter (0-40 cc/min.) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

Note - Carefully release the probe inlet plug before turning off the pump.

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

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

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

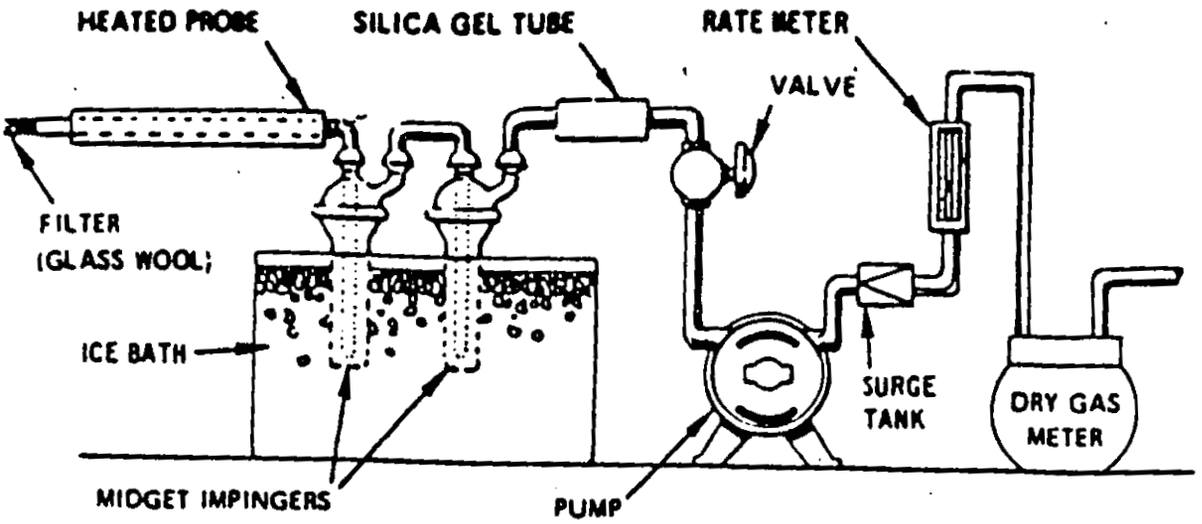


Figure 4.3 Moisture-sampling train - approximation method.

LOCATION _____ COMMENTS

TEST _____

DATE _____

OPERATOR _____

BAROMETRIC PRESSURE _____

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

Figure 4.4 Field Moisture Determination Approximation Method

EEB 04·87

3.3.1 Nomenclature.

B_{wm}	=	Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws}	=	Water vapor in the gas stream, proportion by volume.
M_w	=	Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m	=	Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.
P_{std}	=	Standard absolute pressure, 760 mm Hg (29.92 in Hg).
R	=	Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g-mole) (^oK) for metric units and 21.85 (in Hg) (ft^3)/lb-mole (^oR) for English units
T_m	=	Absolute temperature at meter, ^{o} (^oR).
T_{std}	=	Standard absolute temperature, 293^oK (528^oR).
V_f	=	Final volume of impinger contents, ml.
V_i	=	Initial volume of impinger contents, ml.
V_m	=	Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$	=	Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$	=	Volume of water vapor condensed, corrected to standard conditions, scm (scf).
ρ_w	=	Density of water, 0.9982 g/ml (0.002201 lb/ml).
Y	=	Dry gas meter calibration factor.

3.3.2 Volume of water vapor collected.

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

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

Equation 4-5

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

= 0.04707 ft^3/ml for English units

3.3.3 Gas Volume

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

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

Equation 4-6

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

= 17.65 °R/in. Hg for English units

3.3.4 Approximate moisture content.

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

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

Equation 4-7

4. Calibration

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5; Section 5-3 (metering system); Section 5.5 (temperature gauges); and Section 5.7 (barometer). The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the

5. Bibliography

1. Air Pollution Engineering Manual (Second Edition). Danielson, J.A. (ed.). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP-40. 1973.

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

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

APPENDIX G

CARB Method 410A

Determination of Benzene from Stationary Sources
(Low Concentration Gas Chromatography Technique)

State of California
Air Resources Board

Method 410A

Determination of Benzene from Stationary Sources (Low Concentration Gas Chromatographic Technique)

Adopted: March 28, 1986

METHOD 410A DETERMINATION OF BENZENE FROM STATIONARY SOURCES (LOW CONCENTRATION GAS CHROMATOGRAPHIC TECHNIQUE)

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability: This method applies to the measurement of low concentration emissions of benzene from stationary sources. The method does not account for benzene contained in particulate matter.

1.2 Principle: An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a photo ionization detector (PID).

2. RANGE AND SENSITIVITY

The range of this method is 1.0 to 1000 ppb. The upper limit may be raised by extending the calibration range or by diluting the sample. The lower limit may be improved depending on the skill of the operator and the quality of the equipment.

3. INTERFERENCES

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of benzene; but interferences may be encountered from some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Executive Officer. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Executive Officer.

Note: L = liter

ml = milliliter

ul = microliter

3.1 Information regarding the stationary source being tested, such as the industrial process, fuel, waste material being treated, and other pertinent information should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as benzene at the operating conditions described in this method is a potential interference. Retention time data on a single column cannot be considered proof of chemical identity. If there are significant potential interferences, separate conditions (column packing, temperature, detector, etc.) must be changed to circumvent the problem.

3.3 If other gas chromatagraphic conditions or other techniques are used, the tester is required to substantiate the data through an adequate quality assurance program approved by the Executive Officer.

4. APPARATUS

The following sampling apparatus has been successfully field tested and is recommended. Any other sampling apparatus which, after review of the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

4.1 Sampling (see Figure 1 in part 6. PROCEDURE): The sampling train consists of the following components.

4.1.1 Probe: Stainless steel, Pyrex glass or Teflon tubing (as stack temperature permits), equipped with an optional glass wool plug to remove particulate matter.

4.2 Sample Recovery: Teflon tubing (or other suitably inert material), 6.4 mm outside diameter, is required to connect the sample bag to the chromatograph sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.

4.3 Analysis: The following equipment is needed:

4.3.1 Gas Chromatograph: With PID, potentiometric strip chart recorder and 1.0 to 2.0 ml cryogenic sampling loop with automatic sample valve. The chromatographic system shall be capable of producing a response to 1.0 ppb benzene that is at least as great as the average noise level.

Ths signal to noise ratio shall be reported with all lab results and the following significance shall be inferred:

1:1 information

2:1 detection

3:1 quantification

(Response is measured from the average value of the base line to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns: Columns are as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of benzene standards are not impaired and he has available for review information confirming that there is adequate resolution of the benzene peak. (For the listed or alternative

columns, the resolution goal shall be an area overlap of not more than 10 percent of the benzene peak by an interferent peak. Any such area overlap shall be reported with all lab results.) Calculation of area overlap is explained in Appendix A: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A: Stainless steel, 6 ft. by 1/8 in., packed with 10% N,N-bis (2-cyanoethyl) formamide on 100/120 mesh Chromasorb PAW. The packing is a suspect carcinogen. There are other columns at least as sensitive to benzene.

4.3.2.2 Comumn B: Stainless steel, 6 ft. by 1/8 in., 6C column, packed with 10% 1,2,3 - tris (2-cyanoethoxy) propane.

4.3.3 Flow Meters (2): Rotameter type, 100 ml/min capacity.

4.3.4 Gas Regulators: For required gas cylinders.

4.3.5 Thermometer: Accurate to 1°C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer: Accurate to 5 mmHg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump (optional): Leak-free, with minimum of 100 ml/min capacity.

4.3.8 Recorder: Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter: Optional, in place of disc or electronic integrator, or recorder, to measure chromatograph peak areas.

4.3.10 Syringe: Ground glass, 100 ml, or other suitable device to transfer gas samples from Tedlar bags to the GC sample inlet. Establish background level of benzene concentration in syringe as less than one percent of level measured for test.

4.4 Calibration: Sections 4.4.2 through 4.4.5 are for the optional procedure in Section 7.1.

4.4.1 Syringe: As in 4.3.10. Background level measured for each test.

4.4.2 Tedlar or Aluminized Mylar Bags: 50 L capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringes: 1.0 uL, 10uL, and 100 uL, individually calibrated to dispense liquid benzene.

4.4.4 Dry Gas Meter with Temperature and Pressure Gauges: Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

4.4.5 Midget Impinger/Hot Plate Assembly: To vaporize benzene.

5. REAGENTS

Use only reagents that are of chromatographic grade.

5.1 Analysis: The following are needed for analysis.

5.1.1 Helium or Nitrogen: Zero grade, for chromatograph carrier gas; also, helium is for flushing sample gases.

5.2 Calibration: Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Benzene, 99 Mol Percent Pure: Certified by the manufacturer to contain a minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen, Zero grade: For preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3): Gas mixture standards (500, 50, and 5 ppb benzene in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ±3 percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ±5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified benzene concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification: The manufacturer shall certify the concentration of benzene in nitrogen in each cylinder by (a) directly analyzing

each cylinder and (b) calibrating the analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 5 and 10 ppm) to prepare his calibration curve by an appropriate dilution technique; and (2) a low-concentration calibration standard (between 5 and 10 ppb) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards: Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent benzene) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Bureau of Standards. The agreement between

the initially determined concentration value and the verification concentration value must be within ±5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2): Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (benzene in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm benzene and one high-concentration cylinder in the range of 100 to 300 ppm benzene. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source.

6. PROCEDURE

The following sampling procedure has been successfully field tested and is recommended. Any other sampling procedure which, after review of the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

6.1 Sampling: Assemble the sample train as shown in Figure 1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack, and start the pump with the needle valve adjusted to yield a flow that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. Again connect the sample train as shown in Figure 1 and begin sampling. 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. Keep the bag container in shade.

6.2 Sample Storage: Keep the sample bags out of direct sunlight. Perform the analysis within 4 days of sample collection.

6.3 Sample Recovery/Freezeout/Injection: CAUTION, serial dilutions may be necessary for highly concentrated samples to protect the GC system from overloading.

6.3.1 Sample Recovery: Immerse the sample loops in liquid nitrogen (LN_2) and allow the temperature to stabilize (approximately 5 minutes).

After flushing the 100 ml syringe with about 40 ml of the sample, withdraw 40 ml from the sample bag.

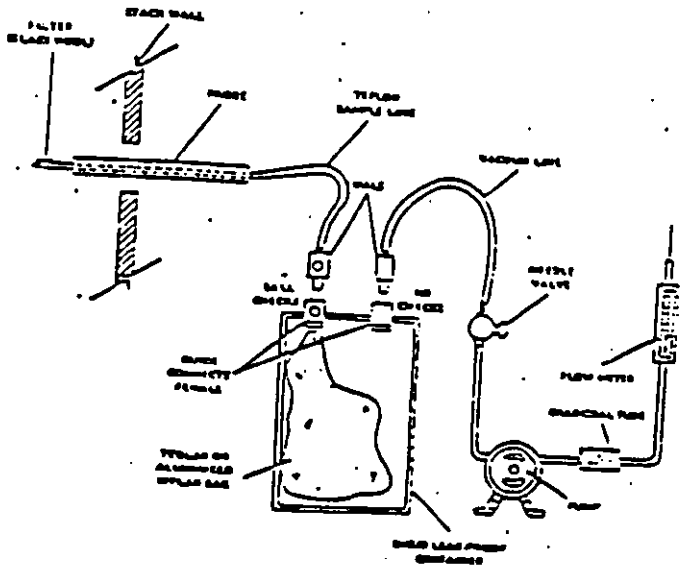


Figure 1

6.3.2 Freeze-out: Transfer the sample into the cryogenic sampling loop (trap).

Back fill the syringe with 40 ml of helium and flush the 40 ml through the trap. then flush helium through the trap for 2 minutes at 20 ml/min.

Stop the helium flushing. Remove the 1/4 inch U-trap from LN_2.

Isolate the cryogenic trap by using an "isolation valve" which allows the carrier gas to by-pass the trap. Replace the LN_2 Dewar with a Dewar containing 80°C water and immerse the trap. Allow all ice to melt from the trap.

6.3.3 Injection: Using the valve, introduce the sample into the carrier gas stream.

6.4 Analysis: CAUTION, serial dilution, may be necessary for highly concentrated samples to prevent overloading. Set the column temperature to ambient for column A or column B, and the detector temperature to 150°C. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. If necessary, adjust flow rate for best detector response. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed, and the

attenuator setting. From the chart, note the peak having the retention time corresponding to benzene, as determined in Section 7.2.1. Measure the benzene peak area, A_m, by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. Use the average value of these two total areas to compute the bag concentration.

6.5 Determination of Bag Water Vapor Content: Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. PREPARATION OF STANDARD GAS MIXTURES, CALIBRATION, AND QUALITY ASSURANCE

7.1 Preparation of Benzene Standard Gas Mixtures: This procedure may only be used if no cylinder standard is available. Assemble the apparatus shown in Figure 2. Evacuate a 50 L Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 L of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling, use the 1.0 uL syringe to inject 1.0 uL of 99+ percent liquid benzene through the septum on top of the impinger. This gives a concentration of approximately 5 ppm of benzene. In a like manner, use the 10 uL and 100 uL syringes to prepare dilutions having approximately 50 ppm and 500 ppm benzene

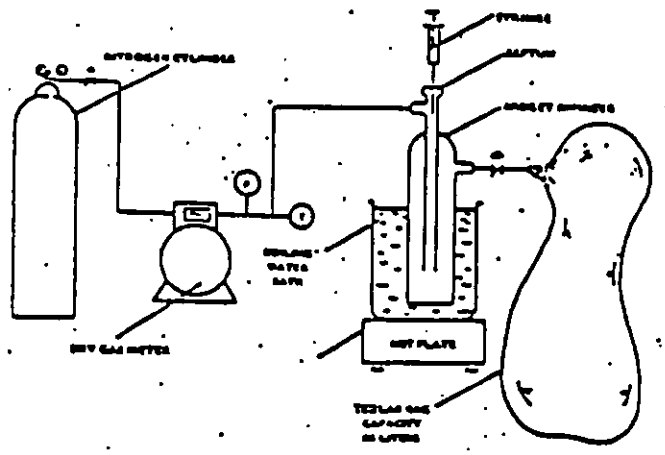


Figure 2

concentrations. Using the same apparatus, the 100 uL syringe, and appropriate dilution techniques, inject 50 mL of each dilution into 3 different empty Tedlar bags and fill each with 50 L of nitrogen to obtain 3 standard gas mixtures of 5, 50, and 500 ppb. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for 7 days from the date of preparation, after which time preparation of new gas mixtures is required. (Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

7.2 Calibration:

7.2.1 Determination of Benzene Retention Time: (This section can be performed simultaneously with Section 7.2.2.) CAUTION, serial dilutions may be necessary for highly concentrated samples to protect GC plumbing. Establish chromatograph conditions identical with those in Section 6.4, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed, and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, and flush the sample loop for 30 sec at the rate of 100 ml/min with one of the benzene

calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve: Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.) using conditions identical with those listed in Sections 6.3 and 6.4. Record C, the concentration of benzene injected, the attenuator setting, chart speed, peak areas, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus C_c. When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after each set of bag samples; whichever is more frequent.

7.3 Quality Assurance:

7.3.1 Analysis Audit: Immediately after the preparation of the calibration curve and before the sample analyses, perform a check for drift against a cylinder of known concentration traceable to the last analysis audit. At least twice a year, perform the analysis audit described in Appendix B: "Procedure for Field Auditing GC Analysis."

7.3.2 Leak Checks: While performance of this section is required after bag use, it is also advised that it be performed before bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H_2O (2 to 4 in H_2O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5 to 10 cm H_2O (2 to 4 in H_2O) and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

7.3.3 Bag Check. To insure no contamination or interferences from the Tedlar bag, a sufficient number of bags should be checked before use. This can be accomplished by filling the bag with

N_2 or zero air & making an injection on the GC under normal analysis conditions. It is recommended that new bags be used each time, but, if this is not possible, it is necessary to check every bag prior to use.

7.3.4 Syringe Check. Prior to use, the GC injection syringe should be checked for contaimination by inserting the needle through the injector septum, drawing a volume of carrier gas into the barrel of the syringe & re-injecting it back onto the column. This procedure should also be done periodically during the analysis to insure no contamination of the syringe.

8. Calculations:

8.1 Optional Benzene Standards Concentrations:

Calculate each benzene standard concentration (C_c in ppm) prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{B(0.2706)(10^3)}{V_m \; Y \; \frac{293}{T_m} \; \frac{P_m}{760}}$$

$$C_c = 701.9 \frac{BT_m}{V_m \; Y \; P_m}$$

where:

B = Volume of benzene injected, microliters.

V_m = Gas volume measured by dry gas meter, liters.

Y = Dry gas meter calibration factor, dimensionless.

P_m = Absolute pressure of the dry gas meter, mmHg.

T_m = Absolute temperature of the dry gas meter, ^oK.

0.2706= Ideal gas volume of benzene at 293° K and 760 mmHg L/ml.

10^3 = Conversion factor [(ppm) (ml)/ul].

8.2 Benzene Sample Concentrations: From the calibration curve described in Section 7.2.2 above, select the value of C_c that corresponds to A_c. Calculate the concentration of benzene in the sample (C_s in ppm) as follows:

$$C_s = \frac{C_c \; P_r \; T_i}{P_i \; T_r \; (1-S_{wb})}$$

where:

C_s = Concentration of benzene in the sample, ppm.

C_c = Concentration of benzene indicated by the gas chromatrograph, ppm.

P_r = Reference pressure, the barometric pressure recorded during calibration, mmHg.

T_i = Sample loop temperature at the time of analysis, ^oK.

P_i = Barometric pressure at time of analysis, mmHg.

Tr = Reference temperature, the sample loop temperature recorded during calibration, ^oK.

S_{wb} = Water vapor content of the bag sample, volume fraction.

Appendix A

Determination of Adequate Chromatographic Peak Resolution

In this method of dealing with resoultion, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from -2 to +2 . This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance, b, one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over limits $b-2\sigma_s$ to $b+2\sigma_s$ where σ_s is the standard deviation of the sample curve.

There are several ways this calculation can be simplified. Overlap can be determined for curves of unit area; then actual areas can be introduced. The desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 Texas Instruments Program Manual STI. 1975, Texas Instruments, Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi\sigma_c}}\int_{b-2\sigma_s}^{b+2\sigma_s} e^{-\frac{t_c^2}{2\sigma_c}}\,dt = \frac{1}{\sqrt{2\pi}}\int_{\frac{b-2\sigma_s}{c}}^{\infty} e^{-\frac{x^2}{2}}\,dx - \frac{1}{\sqrt{2\pi}}\int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{-\frac{x^2}{2}}\,dx$$

The following calculation steps are required:

1. $2\sigma_s = t_s / 2 \ln 2$
2. $\sigma_c = t_c / 2 \ln 2$
3. $x_1 = (b-2\sigma_s)/\sigma_c$
4. $x_2 = (b+2\sigma_s)/\sigma_c$
5. $Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{\frac{x^2}{-2}} dx$
6. $Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{-\frac{x^2}{2}} dx$
7. $I_o = Q(x_1) - Q(x_2)$
8. $A_o = I_o A_c / A_s$
9. Percentage overlap = $A_o \times 100$

where

A_s = The area of the sample peak of interest determined by electronic integration, or by the formula $A_s = h_s t_s$.

A_c = The area of the contaminant peak, determined in the same manner as A_s.

b = The distance on the chromatographic chart that separates the maxima of the two peaks.

H_s = The peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

t_s = The width of the sample peak of interest at 1/2 of peak height.

t_c = The width of the contaminant peak at 1/2 of peak height.

σ_s = The standard deviation of the sample compound of interest elution curve.

σ_c = The standard deviation of the contaminant elution curve.

$Q(x_1)$ = The integral of the normal distribution function from x_1 to infinity.

$Q(x_2)^*$ = The integral of the normal distribution function from x_2 to infinity.

I_o = The overlap integral.

A_o = The area overlap fraction.

In judging the suitability of alternate gas chromatographic columns, or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In those cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, It may be possible to define an effective width for t_c as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

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* In most instances, $Q(x_2)$ is very small and may be neglected.

APPENDIX B
Procedure for Field Auditing GC Analysis.

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. Check that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism of same.

B. At the beginning and conclusion of the audit, record each cylinder number and cylinder pressure. Never analyze an audit cylinder when the pressure drops below 200 psi.

FIELD AUDIT REPORT

PART A - To be filled out by organization supplying audit cylinders

1. Organization supplying audit sample(s) and shipping address

   _____

2. Audit supervisor, organization, and phone number

   _____

3. Shipping instructions: Name, Address, Attention

   _____

   _____

   _____

4. Guaranteed arrival date for cylinders _____

5. Planned shipping date for cylinders _____

6. Details on audit cylinders from last analysis

	Low Conc.	High Conc.
a. Date of last analysis	_____	_____
b. Cylinder number	_____	_____
c. Cylinder pressure, psi	_____	_____
d. Audit gas(es)/balance gas	_____	_____
e. Audit gas(es) ppm	_____	_____
f. Cylinder construction	_____	_____

C. During the audit, the analyst is to perform a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples. Normally, it will be conducted immediately after the GC calibration and prior to the sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analysis and then compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within ± 10 percent, he then directs the analyst to begin the analysis of source samples. Audit supervisor judgment and/or supervisory policy determine course of action if agreement is not within ± 10 percent.

Where a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analyses, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor is to record each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told the actual audit concentrations until the calculated concentrations have been submitted to the audit supervisor.

Part B: To be filled out by audit supervisor

1. Process Sampled _____
2. Location of audit _____
3. Name of individual audited _____
4. Audit date _____
5. Audit results

	Low Conc.	High Conc.
a. Cylinder Number	_____	_____
b. Cylinder Pressure before audit, psi	_____	_____
c. Cylinder pressure, after audit, psi	_____	_____
d. Measured concentrations, ppm Injection #1*	_____	_____
Injection #2*	_____	_____
Average*	_____	_____
e. Actual Audit concentration, ppm (Part A, 6e)	_____	_____
f. Audit Accuracy*	_____	_____
Low Conc. Cylinder	_____	_____
High Conc. Cylinder	_____	_____

*Percent Accuracy = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

g. Problems detected (if any) _____

_____

_____

*Results of two consecutive injections that meet the sample analysis criteria of the test method.

APPENDIX H

CARB Method 421

Determination of Hydrochloric Acid
Emissions from Stationary Sources

State of California
Air Resources Board

Method 421

Determination Of Hydrochloric Acid Emissions From Stationary Sources

Adopted: January 22, 1987

Method 421 - Determination of Hydrochloric acid Emissions From Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method applies to the determination of hydrochloric acid emissions from stationary sources. It does not measure liquid or solid phase chloride. Gaseous HCl is defined as that which passes the filter at its heated temperature.

1.2 Principle

Particulate and gaseous chloride emissions are extracted isokinetically from the stack and passed through an impinger-filter train where the gaseous chloride is collected in a solution of Sodium Bicarbonate and Sodium Carbonate. This impinger solution is analyzed for chloride by ion chromatography with conductivity detection. The chloride peak is identified by characteristic retention time, and quantified by reference to external standards.

2. RANGE, SENSITIVITY, AND PRECISION

2.1 Range and Sensitivity

The analytical method has been used to measure chloride concentration in drinking water, surface water, and mixed domestic and industrial wastewater. (See Reference 10.1).

A method detection limit (MDL) of 0.015 mg/L has been obtained with reagent water at an attenuator setting of 1 uMHO full scale (Reference 10.1). Any change in this setting would produce a proportional change in the MDL. The MDL would also vary with the sample matrix.

2.3 Precision

The following single operator accuracy and precision data were obtained for reagent(RW), drinking(DW), and surface (SW) water, and mixed domestic and industrial wastewater (WW) (Reference 10.1).

Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
RW	0.050	7	97.7	0.047
DW	10.0	7	98.2	0.289
SW	1.0	7	105.0	0.139
WW	7.5	7	82.7	0.445

3. INTERFERENCES

The chromatographic columns and the corresponding operating parameters herein described normally provide a high degree of resolution; but interferences may be encountered from some sources. Therefore, the chromatograph operator shall select column and operating parameters best suited to the particular analytical problem, subject to approval by the Executive Officer. This approval is automatic provided that the tester produces data to demonstrate that the technique is capable of accurate and reproducible measurements, and has the data available for review by the Executive Officer.

3.1 Any anion with a retention time similar to that of chloride can interfere. Large amounts of an adjacent anion can interfere with the peak resolution for the chloride anion. Sample dilution and/or spiking can solve most interference problems.

3.2 Contaminants in the reagent water, reagents, glassware and other sample processing apparatus can cause discrete artifacts or elevated baseline in ion chromatograms.

3.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns must be filtered to prevent damage to instrument columns and flow systems.

3.4 The "water dip" or negative peak elutes near to the chloride peak and can interfere. When the standard eluent (Section 5.4.2) does not give adequate separation of the chloride peak from the water dip, the recommended eluent is 2mM NaOH/2.4mM $NaHCO_3$ (Reference 10.3).

3.5 If other ion chromatographic conditions or other techniques are used, the tester is required to substantiate the data through an adequate quality assurance program approved by the Executive Officer.

4. APPARATUS

The following sampling apparatus is recommended. The tester may use an alternative sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

4.1 Sampling Train
A schematic diagram of the sampling train is shown in Figure 1. The equipment required for this train is the same as described in Section 2.1 of CARB Method 5 except as follows:

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

4.1.2 Impingers. Four impingers are connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design modified by replacing the tip with a 1-cm (0.5 in.) I.D. glass tube extending to 1 cm from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.
The first and second impingers shall contain known quantities of 3 mM sodium bicarbonate ($NaHCO_3$), and 2.4 mM sodium carbonate (Na_2CO_3). The third shall be empty, and the fourth shall contain a known weight of silica gel or equivalent dessicant.
A thermometer which measures temperatures to within 1°C (2°F), should be placed at the outlet of the fourth impinger.

4.2 Sample Recovery.
The following items are needed:

4.2.1 Probe Liner and Probe Nozzle Brushes, Petri Dishes, Plastic Storage Containers, Funnel and Rubber Policeman. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.6, and 2.2.7, respectively.

4.2.2 Wash Bottles (2). Only glass may be used.

4.2.3 Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for impinger and probe solutions and washes, 1000 mL. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to chemical attack by 1.0 N NaOH (Narrow mouth glass bottles have been found to be less prone to leakage).

4.2.4 Graduated Cylinder and/or Balance. To measure condensed water to within 2 mL or 1 g. Use a graduated cylinder that has a minimum capacity of 500 mL, and subdivisions no greater than 5 mL. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less).

4.2.5 Funnel. To aid in sample recovery. Only glass may be used.

4.3 Analysis

The following equipment is needed:

4.3.1 Balance - Analytical. Capable of accurately weighing to the nearest 0.0001 g.

4.3.2 Sample bottles. Glass. Of sufficient volume to allow replicate analyses of the anion of interest.

4.3.3 Pipettes. An assortment of sizes.

4.3.4 Volumetric Flasks. 100-mL, 250-mL and 1000-mL.

4.3.5 Ion chromatograph. Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed air, detector, and strip chart recorder. A data system is recommended for peak integration. The ion chromatograph should have at least the components listed below. The analyst may use alternative components provided that there is adequate resolution of the chloride peak, and there is no impairment of the precision and accuracy of the analysis of the chloride standards.

4.3.5.1 Anion guard column: 4 x 50 mm, Dionex P/N 03827, or equivalent.

4.3.5.2 Anion separator column: 4 x 250 mm, Dionex P/N 35350, or equivalent.

4.3.5.3 Anion suppressor column: fiber, Dionex P/N 35350, or equivalent.

4.3,5.4 Pump capable of maintaining a steady flow as required by the system.

4.3.5.5 Flow gauges. Capable of measuring the specified system flow rate.

4.3.5.6 Detector - Conductivity cell. Approximately 6 uL volume, Dionex, or equivalent.

4.3.6 Filtering System. 0.45 micron millipore filter and millipore vacuum filtration unit or equivalent.

5. REAGENTS

Unless otherwise specified, use American Chemical Society reagent grade (or equivalent) chemicals throughout. Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board.

5.1 Sampling.
The following reagents are needed:

5.1.1 Filters, Silica Gel, Crushed Ice and Stopcock Grease. Same as Method 5, Sections 3.1.1, 3.1.2, 3.1.4 and 3.1.5, respectively.

5.1.2 Water. Deionized, distilled, to conform to ASTM Specification D1193-77, Type 3 (Reference 10.1). If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

5.1.3 Impinger Solution. Sodium Bicarbonate 3 mM, and Sodium carbonate 2.4 mM. Dissolve 1.0081 g sodium bicarbonate ($NaHCO_3$) and 1.0176 g of sodium carbonate (Na_2CO_3) in reagent water (5.1.2), and dilute to 4 liters.

5.3 Sample Recovery.

5.3.1 Recovery solvent. Solution of Sodium bicarbonate (3 mM) and Sodium carbonate (2.4 mM). Same as 5.1.3 above.

5.4 Analysis. The following reagents are needed:

5.4.1 Reagent water. Same as 5.1.2 above. Verify that the conductance is 1 uS or less if your system includes a conductivity detector. For other detector options, you must use other methods to monitor your water quality.

5.4.2 Eluent solution: Same as 5.1.3 above.

5.4.3 Sulfuric acid. Concentrated.

5.4.4 Regeneration solution (fiber suppressor). Sulfuric acid, 0.025 N. Dilute 2.8 mL concentrated sulfuric acid (H_2SO_4) to 4 liters with reagent water (same as 5.4.1 above).

5.4.5 Stock Standard Solution, 1000 mg/L. This may be purchased as a certified solution or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as follows:
Dissolve 1.6485 g sodium chloride (NaCl) in reagent water (5.1.2) and dilute to 1 liter. Stock standards are stable for at least one month when stored at 4°C.

5.4.6 Intermediate Stock Standard. Pipet 200 mL of the stock standard (5.4.5 above) into a 1000-mL volumetric flask, and dilute to volume with reagent water (5.4.1). This standard may be stored for one month.

5.4.7 Calibration Standards. Add accurately measured volumes of the intermediate standard to a volumetric flask and dilute to volume with reagent water. Dilute working standards should be prepared weekly.

6. PROCEDURE

6.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedures in order to ensure reliable results.

6.1.1 Pretest Preparation. Follow the same general procedure described in Method 5, Section 4.1.1, except the filter need not be weighed.

6.1.2 Preliminary Determinations. Follow the same general procedure described in Method 5, Section 4.1.2.

6.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 mL of impinger solution (5.1.3) in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Assemble the train as shown in Figure 1.

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

6.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in ARB Method 5, Figure 5-2.

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

6.2 Sample Recovery.
Allow the probe to cool. Inspect the train prior to and during disassembly and note any abnormal conditions. Disconnect the impingers, and treat them in the following manner:

6.2.1 Container No. 1 (Impingers). If the volume of liquid is large, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease and cap the joints.

2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

3. Transfer the contents of the impingers to a 500-mL graduated cylinder. Remove the outlet ball joint cap and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within ±2 mL. Alternatively, determine the weight of the liquid to within ±0.5 g. Record in the log the volume or weight of the liquid present, and the occurrence of any color or film in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).

4. Transfer the contents to Container No. 1.

5. Note: In steps 5 and 6 below, measure and record the total amount of recovery solvent used for rinsing. Pour approximately 30 mL of recovery solvent (5.3.1) into each of the first three impingers and agitate the impingers. Drain the recovery solvent through the outlet arm of each impinger into Container No. 1. Repeat this operation a second time; inspect the impingers for any abnormal conditons.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with recovery solvent. Transfer this rinse into Container No. 1. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

6.2.2 Container No. 2 (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent, and note its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel, and rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or any other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the procedure for Container No. 2 under Section 6.4 (Analysis).

6.2.3 Recovery Solution Blank. Save a total volume of recovery solution equal to that used for sampling (impinger solution) and cleanup (6.2.1). Place in a glass sample container, and seal the container.

6.3 Sample Preparation.

6.3.1 Container No. 1 (Impingers). Check the liquid level to determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or determine the volume lost from the difference between the initial and final solution levels, and use this value to adjust the final results, subject to approval by the Executive Officer. Filter the sample through a Millipore membrane filter (4.3.6) into a volumetric flask, and dilute to volume with deionized distilled water.

6.3.2 Recovery Solution Blank. Filter through a Millipore membrane filter (4.3.6) into a volumetric flask. Dilute to the same volume as the sample (Section 6.3.1 above).

6.4 **Analysis.**

The method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 7.3.2.

6.4.1 The following operating conditions are recommended for the ion chromatograph. Other columns, chromatographic conditions, or detectors may be used if the conditions of Section 7.3.2 are met.

6.4.1.1 Columns. As specified in 4.3.5.

6.4.1.2 Detector. As specified in 4.3.5. Select the sensitivity required for the analysis. Follow the manufacturer's instructions for obataining the optimum temperature compensating factor for each column set and eluent batch. This is especially important when operating at high sensitivities.

6.4.1.3 Eluent. As specified in 5.4.2.

6.4.1.4 Sample Loop - 100 uL.

6.4.1.5 Pump Volume - 2.30 mL/min.

Calibrate the ion chromatograph, and prepare a calibration curve as described in Section 7.2.

6.4.2 Load and inject a fixed amount of well mixed sample (at least 10 loop volumes). The first sample to be analyzed should be a quality control standard sample. Use the same size loop for standards and samples. Flush the injection loop thoroughly, with each new sample. An automated constant volume injection system may also be used.

For each sample, record the injection time, injection volume, flow rate, detector sensitivity setting, recorder chart speed, peak height or area, and retention time. Repeat two times, or until two consecutive values for the chloride peak do not vary by more than 5 percent. From the average of these two values, subtract the peak height or area of the recovery solution blank. Use the corrected sample value to compute the chloride concentration of the sample. If the chloride concentration of the absorbing solution blank is below the working range of the analytical method, use zero for the blank.

If the peak response exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

Run a reagent blank and a standard after every 10 samples to check the chromatograph calibration. Recalibrate as necessary.

The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for chloride. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

If the resulting chromatogram fails to produce adequate resolution, or if identification of chloride is questionable, spike the sample with an appropriate amount of standard, and reanalyze.

6.4.3 Container No. 2 (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7. CALIBRATION, STANDARDIZATION, AND QUALITY CONTROL

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

7.2 Standard Calibration Curve. Establish the ion chromatographic operating parameters indicated in Section 6.4.1 above. Prepare a sufficient number of standards to allow calculation of an accurate calibration curve. This should include a minimum of three chloride calibration standards and a blank (Section 5.4.6). The concentration of one of the standards should be near, but above the method detection limit if the system is being operated on an attenuator setting that allows this measurement. The other standards should correspond to the range of concentrations expected in the sample, or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

7.2.1 Pump eluent through the column. After the system is equilibrated, and the detector baseline is stable, inject the highest standard. Adjust zero to approximately 10 percent of chart. As the highest standard for chloride elutes, adjust the calibration to approximately 90 percent of chart.

7.2.2 Inject 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard starting with the highest concentration. Record the concentration of the standard, peak height or area, the injection time (the position of the pen on the chart at the time of sample injection), injection volume, flow rate, attenuator setting, and recorder chart speed. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the chloride retention time. Repeat the injection at least two times or until 2 consecutive values for the chloride peak area are within 5 percent of their average value. When all the standards have been similarly analyzed, subtract the average peak height or peak area of the blank from the averaged peak heights of each standard. Calculate a linear regression plot of the corrected peak height of each standard (y-axis) versus the corresponding concentration (x-axis).

7.3 Quality control

7.3.1 The minimum quality control requirements are an initial demonstration of laboratory capability (according to Section 7.3.2), and the analysis of spiked samples as a continuing check on performance. The laboratory should maintain performance records to document the quality of data that are generated.

In recognition of the rapid advances occuring in chromatography, the analyst is permitted certain options to improve separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure described in Section 7.3.2 below.

The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. Field and laboratory duplicates should also be analyzed.

7.3.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory control standard.

7.3.2.1 Select a representative spike concentration. Use the stock standard to prepare a quality control check sample with concentration in reagent water that is 100 times greater than the value selected above.

7.3.2.2 Use a pipet to add 1.00 mL of the check sample (7.3.2.1) to each of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure in Section 6.4.2.

7.3.2.3 Calculate the average percent recovery (R), and the standard deviation (s) of the percent recovery, for the results.

7.3.2.4 Compare these results (7.3.2.3) with the recovery and single operator precision expected for the method (Section 2.3). If the data are not comparable within control limits (7.3.3), review the potential problem areas and repeat the test.

7.3.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration of analyte being measured.

7.3.3.1 Calculate upper and lower control limits for method performance as follows:
Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s
where R and s are calculated as in Section 7.3.2.3. The UCL and LCL can be used to construct control charts that can be used to follow trends in performance.

7.3.4 The accuracy statement for the method may be written as R $\pm$ s where R and s are as defined in Section 7.3.2.3. This statement should be developed from analyses of at least four samples prepared according to Section 7.3.2.3.

7.3.5 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences will not pose a problem. Whenever there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

7.3.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive would depend to some degree on the nature of the samples.

7.3.6.1 Field duplicates may be analyzed to monitor the precision of the sampling technique.

7.3.6.2 When there is doubt about the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and spiking must be used.

7.3.6.3 Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

8. CALCULATIONS.

8.1 Nomenclature.

C_c = corrected chloride concentration (ug/mL) from the calibration curve.

C_s = concentration of HCl in the stack gas (mg/m^3), dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293 ^oK (528^oR).

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

V_s = Total volume of sample (mL) after dilution (from Section 6.3.1).

m_t = Total HCl (mg) in sample volume V_s.

$V_{m(std)}$ = Dry Gas Volume. dscm (dscf). See Section 8.2 below.

8.2 Dry Gas Volume.
Using the data from this test, calculate $V_{m(std)}$, the total volume of dry gas metered corrected to standard conditons (20°C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{m(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

8.3 Volume of Water Vapor and Moisture content.
Using data obtained in this test and Equations 5-2 and 5-3 of Method 5, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas.

8.4 Concentrations.

8.4.1 Total Hydrochloric Acid in Sample. Use the following equation to calculate the mass of HCl in the sample volume V_s:

$$m_t = \frac{C_c \times 10^{-3} \times V_s \times 1.028}{F} \qquad \text{Eq. 1}$$

Where:

1.028 = the conversion from chloride anion to hydrochloric acid

8.4.2 Hydrochloric Acid Concentration in Stack Gas. Use the following equation to calculate HCl concentration in the stack gas:

$$C_s = \frac{K\ m_t}{V_{m(std)}} \qquad \text{Eq. 2}$$

Where:

$K = 35.31\ ft^3/m^3$ if $V_{m(std)}$ is expressed in English units

$K = 1.00\ m^3/m^3$ if $V_{m(std)}$ is expressed in metric units

8.5 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively. To calculate V_s the average stack gas velocity, use equation 2-9 of Method 2 and the data from this field test.

9. ALTERNATIVE TEST METHODS FOR INORGANIC CHLORIDE

9.1 NIOSH Method 7903. Issued 2/15/84 (Reference 10.4). This method has been developed for the determination of the total concentration of airborne inorganic anions after collection as their corresponding acids on a silica gel sorbent sampler tube with glass fiber plug. The analytical technique is ion chromatography, and will therefore be subject to the same interferences reported in Section 3 of this method. Analytical precision estimates have been obtained with laboratory generated mixtures of acids. The measurement precision was 0.025, and the overall precision was 0.059 for HCl in the concentration range 0.14 - 14 mg/m^3.
However, the effectiveness of the sampling method for HCl has not been demonstrated.

9.2 NaOH Impinger sampling train (Reference 10.5)
A midget impinger sampling train with 1.0 N NaOH as the impinger solvent was used to sample coal-fired boilers and municipal incinerators. Collection efficiencies were satisfactory, but pretreatment of the sample was necessary to avoid SO_3^{2-} and cation interferences with the quantitative method, which consisted of a titration of chloride with a standard $Hg(NO_3)_2$ solution using a bromophenol blue-diphenylcarbazone mixed indicator.

10. BIBLIOGRAPHY.

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

10.2 O'Dell, J.W., Pfaff, J.D., Gales, M.E., and McKee, G.D. "Test Method: The determination of Inorganic Anions in water by Ion Chromatography - Method 300.0. U.S. Environmental Protection Agency/Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Jan., 1984.

10.3 U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., Method 9250. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1982).

10.4 NIOSH Manual of Analytical Methods, 3rd ed., Method 7903, Acids, Inorganic. U.S. Department of Health and Human Services DHHS (NIOSH) Publ. No. 84-100. Feb, 1984.

10.5 Cheney, J.L., and Fortune, C.R., 1979. Evaluation of a method for measuring hydrochloric acid in combustion source emissions. The Science of the Total Environment. 13: 9 - 16.

10.6 Dionex, System 2000 i/SP. Ion Chromatograph. Operation and Maintenance Manual. Document No. 32584-01. March 1985. Dionex Corp. Sunnyvale, California 94086.

10.7 Same as Method 5, Citations 2 to 5 and 7 of Section 7.

APPENDIX I

CARB Method 422

Determination of Halogenated Organics Emissions
from Stationary Sources

State of California
AIR RESOURCES BOARD

Method 422

Determination of Halogenated Organics Emissions from Stationary Sources.

Adopted: January 22, 1987

METHOD 422 DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

This method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, or by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. PRINCIPLE AND APPLICABILITY

1.1 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a suitable detector.

1.2 Applicability. The method is applicable to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, trichlorotrifluoroethane, and ethylene dibromide in stack gases. It is not applicable where the gases are occluded in particulate matter.

2. RANGE AND SENSITIVITY

The procedure described herein is applicable to the measurement of halogenated organics in the 0.1 to 200 ppm range. The upper limit may be extended by further calibration or by dilution of the sample. The lower limit may be extended by injection of larger sample volumes or by preconcentration techniques.

3. INTERFERENCES

The chromatography column with the corresponding operating parameters herein described has been represented as being useful for producing adequate resolution of halogenated organics. However, resolution interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of the particular compound of interest without reducing the response to that compound, as specified in Section 4.3.1

If other gas chromatographic conditions or other techniques are used, the tester is required to substantiate the data through an adequate quality assurance program which is subject to approval by the Executive Officer.

4. APPARATUS

4.1 Sampling (see Figure 1)

The following sampling apparatus has been successfully field tested and is recommended. Any other sampling apparatus which, after review by the Executive Officer, is deemed equivalent for the purposes of this test method, may be used. Apparatus required for sampling is described below. It is recommended that all equipment which comes in contact with sampled gas be of stainless steel, glass, teflon, or tedlar unless these materials are found unsatisfactory and other materials demonstrated suitable in specific situations.

4.1.1 Probe. Stainless steel, Pyrex glass or Teflon as appropriate for stack temperature, equipped with a glass wool plug to remove particulate matter. A permanently plumbed, valved connection to a duct or stack may be used instead of a probe.

4.1.1.1 An impinger with an ice bath may be required to trap condensation in certain cases; if used it shall be located between the probe and the sample line shown in Figure 2.

4.1.2 Sample line. Teflon tubing, 6.4 mm (1/4 inch) outside diameter, of length sufficient to connect the probe to bag and not longer than 100 ft.

4.1.2.1 To reduce the risk of sample contamination, new unused tubing shall be used for each series of bag samples considered to constitute an emissions test.

4.1.3 Threaded, sealed couplings shall be used to connect sample train components. Quick-connect couplings of stainless steel, some with ball checks which prevent flow when disconnected and some without ball checks, are recommended as shown in Figure 1.

4.1.4 Sample bags.

4.1.4.1 Bags shall be made of Tedlar film.

4.1.4.2 Stainless steel quick-connect couplings with ball checks as shown in Figure 1 are recommended but manually valved fittings may be used.

4.1.4.3 All bags used in a testing program or project shall be uniform and free from differences in manufacture or construction

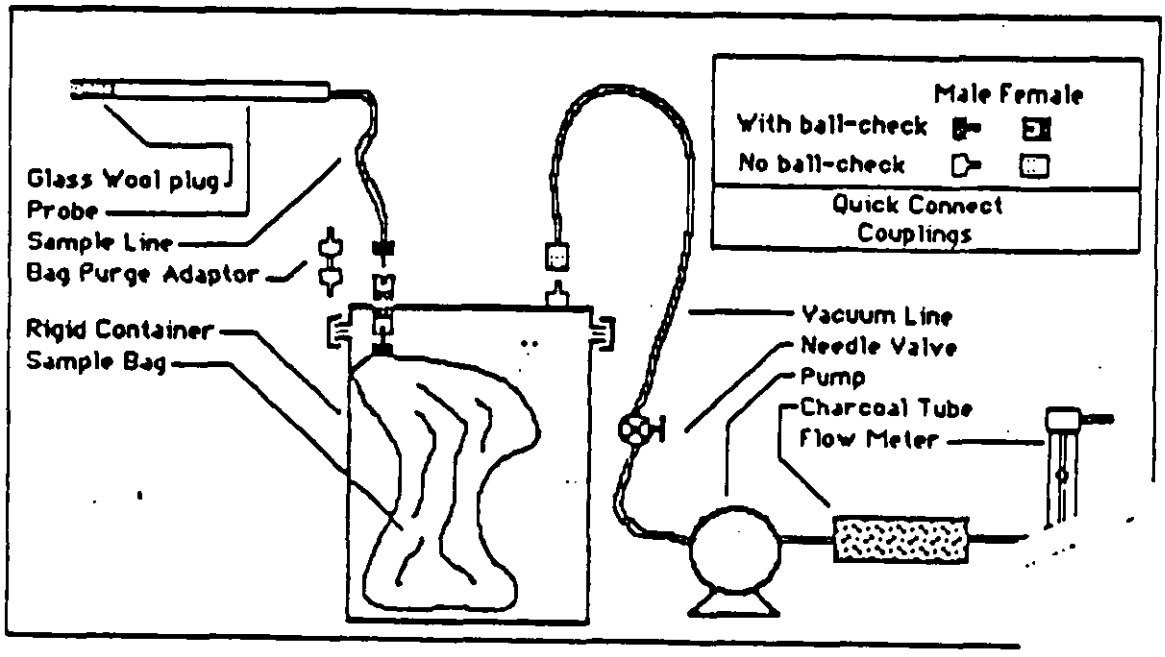


Figure 1 – Recommended Sampling Train

which could affect compatibility with pollutants of interest.

4.1.5 Rigid container(s) for filling sample bags by application of vacuum.

4.1.5.1 The container shall be airtight when sealed but need not be specially constructed for the purpose; cardboard cartons and duct tape have been used effectively.

4.1.5.2 The container shall be opaque except that a small window to check the condition of the bag within is permissible.

4.1.5.3 The container shall be fitted with couplings to mate with sample bags, sample line and vacuum line and with provisions to shut off vacuum and sample; quick-connect couplings as shown in Figure 1 are recommended.

4.1.5.4 The container shall have an internal capacity no larger than the sample bags used.

4.1.5.5 Sample bags may be fabricated with rigid containers as an integral unit.

4.1.6 Double-ended adaptor to allow connection of vacuum line to either sample line or rigid container inlet.

4.1.7 Needle valve to adjust sample flow rate.

4.1.8 Pump, leak free, with capacity of at least 2 liters per minute.

4.1.8.1 A bypass from pump outlet to inlet with an appropriate vacuum relief valve is suggested to protect bags and rigid container.

4.1.9 Charcoal tube to reduce risk of discharging toxic gas mixtures in vicinity of sampling personnel.

4.1.10 Flow meter, rotameter type or equivalent, with measurement range of 0.1 to 1.0 liters per minute for observing sampling rate.

4.1.11 Tube and fittings to connect sample train as shown in Figure 2.

4.1.12 Shipping cartons to protect bags in transport.

4.1.13 Cartons shall be opaque to protect bags from ultraviolet light.

4.1.14 Cartons shall have no staples or metal closures which might damage bags.

4.1.15 The rigid container in which bags are filled may be used for bag transport; any window in the container shall be covered with opaque material during such use.

4.2 Apparatus for Preparation of Known Mixtures.
The apparatus shown in Figure 2 may be useful for preparation of known concentrations of pollutants of interest required in 6 below.

4.3 Aliquot Transfer Adaptor.
A purgeable adaptor to connect analytical apparatus and sample bag fittings for the purpose of withdrawing aliquots of the sample will be required. Withdrawal of aliquots by penetration of the bag film with a syringe needle is not permissable. Specification of analytical apparatus is beyond the scope of this method.

4.4 Expendable Materials

4.4.1 Zero air or 99.999% nitrogen in cylinder(s).

4.4.2 Pure pollutant materials certified by the manufacturer to be 99+% pure for preparation of known mixtures, or appropriate cylinder gases containing the pollutant(s) of interest in known concentration.

4.4.3 Pure distilled water.

4.4.4 Sulfuric acid solution, 0.1 Normal.

4.4.5 Sodium hydroxide solution, 0.1 Normal.

4.4.6 Ice for ice bath.

4.5 Analysis.

4.5.1 Gas Chromatograph. With a suitable detector, potentiometric strip recorder or equivalent such as a data system and 1.0 to 2.0 ml sampling loop in automatic sample valve. Gas tight syringes may be used when an automatic sampling valve and loop are not available. The chromatographic system shall be capable of producing a response where 0.1ppm of the halogenated organic compound of interest is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.5.2 Chromatographic Column. Stainless Steel, 3.05m x 3.2mm, containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. This particular column will not adequately resolve Ethylene Dibromide. An alternative column must be used. CARB Haagen-Smit Method 100 (9.6) uses a glass column, 6ft x 1/4 in 0.2 percent Carbowax 1500 on Supelco 80/100 mesh Carbopac C. in conjunction with an electron capture detector (ECD). Other columns can be used, provided that the precision and accuracy of the analysis of standards are not impaired. Information confirming that adequate resolution of the halogenated organic compound peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak.

4.5.3 Flow Meters (2). Rotameter type, 0 to 100 mL/min capacity.

4.5.4 Gas Regulators with metal diaphragms. For required cylinders.

4.5.5 Thermometer. Accurate to one degree centigrade,

to measure temperature of heated sample loop at time of sample injection.

4.5.6 Barometer. Accurate to 5mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.5.7 Pump--Leak-free. Minimum capacity 100mL/min.

4.5.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.5.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.5.8 to measure chromatograph peak areas.

4.6 Calibration. Sections 4.6.2 through 4.6.5 apply when cylinder standards are not available, and the analyst must prepare standard gas mixtures according to Section 7.1.

4.6.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.6.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration.

4.6.3 Syringes. 25uL, 50uL gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.6.4. Dry Gas Meter, with Temperature and Pressure Gauges. Accurate to ± 2 percent, to meter nitrogen for preparing standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.6.5. Midget Impinger/Hot Plate Assembly. To vaporize solvent.

5. REAGENTS

It is necessary that all reagents be of chromatographic grade.

5.1 Gases for the Gas Chromatograph.

5.1.1. Carrier Gas. Hydrocarbon free, or zero grade helium or 99.999% nitrogen or as recommended by the manufacturer for operation of the detector and compatability with the column.

5.1.2. Fuel. As recommended by the manufacturer for the operation of the GC.

5.1.3. Zero Gas. Hydrocarbon-free air or 99.999% nitrogen, to be used for dilutions, blank

preparation, and standard preparation.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Halogenated organic compound, 99 mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 7.1

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1

5.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen) for which the gas composition has been certified with an accuracy of ± 3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder over which the concentration does not change by greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified concentration of the halogenated organic compound and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be used directly to prepare a chromatograph calibration curve as described in Section 7.2.2.

5.2.3.1 Cylinder Standards Certification. The concentration of the halogenated organic compound in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 200 and 400 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 50 and 100 ppm) for verification of the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low concentration standard exceeds 5 percent of the true concentration, determine the

source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures, and verified by (1) comparing it to gas mixtures prepared (with 99 mol percent of the halogenated organic compounds) in accordance with the procedure described in Section 7.1.1 or (2) by having the calibration standard analyzed by the National Bureau of Standards, if such analysis is available. The agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent. All calibration standards must be reverified on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards prepared identically to those in Section 5.2.3 (the halogenated organic compounds of interest, in nitrogen), except the concentrations are known only to the person supervising the analysis of samples. The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 25 to 50 ppm, and one high-concentration cylinder in the range of 200 to 300 ppm. Other concentration ranges should be considered when the method range is different from the range stated in Section 2. When available, audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternative source must be secured.

6. PROCEDURE

6.1 Requirements for Demonstration of Method Suitability.

6.1.1 Availability of Analytical Capability and Standards. Availability of appropriate analytical services capable of determining concentration(s) of the specific pollutant(s) of interest should be verified.

6.1.2 Preliminary Performance Checks Required. The suitability of this sampling method shall be assessed before sampling any source.

6.1.2.1 The Preliminary Pollutant/Apparatus Compatibility Check described below or equivalent experiments shall be performed before sampling any source. This sampling method shall be considered appropriate only if levels of contamination and change in concentration of non-blank samples demonstrated by these checks are acceptable in the context of testing requirements.

6.1.2.2 The Impinger Effects Check described below or equivalent experiments shall be performed before sampling any source where condensation in the sample line or bag may occur. Use of an impinger in the sampling train will be appropriate only if the percent loss demonstrated by the check is acceptable in the context of testing requirements.

6.1.3 Pre-test Performance Checks Required.

6.1.3.1 All bags shall be subjected to the Pre-test Bag Leak Check described below before use.

6.1.3.2 Sample analyses shall not be corrected for contamination levels found unless it is demonstrated that contamination is predictable and that contamination and sampled concentrations are in fact cumulative.

6.1.4 Incidental Performance Checks Recommended. The Incidental Contamination and Sample Stability Check described in 6.2.5 below is recommended as routine practice to guard against contamination and concentration loss problems which may develop unexpectedly. Other types of quality control checks may also be performed.

6.2 Performance Checks.

6.2.1 Preliminary Pollutant/Apparatus Compatibility Checks. Draw pure air or nitrogen from one bag to another through a 100 ft. long teflon line using procedures similar to those in 6.2.5 below to obtain a blank sample. Repeat to obtain replicates. Draw pure air or nitrogen containing known concentration(s) of the pollutant(s) of interest from one bag to another through the same 100 ft. long Teflon line using procedures similar to those in 6 below. Repeat to obtain replicates. Retain the bag samples for at least 10 days in a shipping carton at room temperature

in a well ventilated area, then analyze to determine final concentration. Report original concentration(s) and concentation(s) after transfer and storage for all samples and percent gain or loss for non-blank samples.

6.2.1.1 Pure air or nitrogen containing known concentration(s) of the pollutant(s) of interest may be prepared using apparatus similar to that shown in Figure 2 to introduce known volumes of the dilution gas and of the pure pollutant, vaporized by heat if necessary, into a bag; stability of such bagged mixtures may be investigated by comparing aged mixtures to freshly prepared mixtures analytically.

6.2.1.2 Alternatively, appropriate gas mixtures in cylinders may be used if available.

6.2.2 Preliminary Impinger Effects Checks. Draw pure air or nitrogen containing known concentration(s) of the pollutant(s) of interest from one bag to another through an impinger filled with pure distilled water and immersed in an ice bath; analyze to determine any loss of concentration(s). Repeat with impingers filled with 0.1N solutions of H_2SO_4 and NaOH. Report percent gain or loss in concentration due to each impinger solution.

6.2.2.1 If pollutant(s) of interest are found to be absorbed regardless of pH and methods exist to quantify the pollutant(s) in solution the stability of the pollutant(s) in solution may be investigated.

6.2.3 Pre-test Bag Leak Check. Check all sample bags for leaks by inflating with zero air or 99.999% nitrogen to 2 to 4 inches of water; good bags should hold constant pressure as indicated by a manometer for 10 minutes or (alternative test) should remain taut and inflated overnight. Report bag acceptability; destroy or repair and retest defective bags.

6.2.4 Pre-test Bag Contamination Check. Check bags for contamination by filling them with zero air or 99.999% nitrogen and subjecting to analysis for the pollutant(s) of interest; contamination in a group of bags may be checked by filling one bag at least half full of zero air or 99.999% nitrogen and .pa drawing the gas from that bag into other bags successively one after another, using procedures similar to those in 6.2.5 below, then

analyzing the last bag filled. Report contamination as concentration(s) found.

6.2.5 Incidental Contamination and Sample Stability Checks. Carry at least one bag filled with zero air or 99.999% nitrogen and at least one bag filled with zero air or 99.999% nitrogen containing known concentration(s) of the pollutant(s) of interest to the sampling site with other equipment and deliver them for analysis with bags containing sampled gas.

6.3 Field Sampling Procedures.

6.3.1 Determine stack moisture content by ARB Method 4; if moisture content is above the 60°F saturation level an impinger is required to control condensation.

6.3.1.1 Sampling shall not be performed if use of an impinger is inappropriate and condensation is expected in the sample.

6.3.2 Assemble the sampling train at the sampling site as shown in Figure 1; if appropriate and necessary, provide an impinger in an ice bath to prevent condensation in the sample.

6.3.3 Leaving the vacuum line unconnected, start the pump and adjust the needle valve to give a flow rate that will at least half-fill the sample bag during the desired sampling period.

6.3.4 Leak check the sample line and the probe or permanent stack connection by closing the intake with a plug or valve and connecting the vacuum line directly to the sample line; consider continuing flow after line evacuation indicative of leakage.

6.3.5 Place the end of the probe in a position to draw a representative sample from the stack if a permanent stack connection is not used.

6.3.5.1 Some risk of exposure to toxic materials may be associated with probe manipulation; protect personnel as necessary.

6.3.6 Purge the sample line. Connect the sample line directly to the vacuum line and draw sufficient gas from the stack through the sample line to purge it.

6.3.7 Prepare to purge the sample bag and its connection to the rigid container by one of the following two methods.

6.3.7.1 Partially fill the sample bag in advance with pure air or nitrogen.

6.3.7.2 Partially fill the sample bag with gas drawn through the sample line from the source to be sampled.

6.3.8 Reconnect the first sample line and then the vacuum line as shown in Figure 1 to begin sampling, noting the time that the rigid container is first subjected to vacuum.

6.3.9 Adjust the needle valve as necessary during sampling to maintain constant sample flow.

6.3.10 Continue sampling for the planned interval and then disconnect the vacuum line noting the time when vacuum on the rigid container is broken.

6.3.11 Promptly disconnect the sample line; ensure that flow through the bag inlet is blocked.

6.3.12 Open the rigid container and remove the sample bag; ensure that the bag fitting is sealed.

6.3.13 Promptly place the sealed bag in a shipping carton; close the carton to prevent possible degradation of the sample by ultraviolet light. Several bags may be placed in the same shipping carton.

6.3.14 Post-test Purge of Sampling Equipment. Draw ambient air through the sample line and pump before disassembling the sample train to reduce the risk of exposing personnel to toxic compounds.

6.4 Sample Bag Transport Procedure.

6.4.1 Transport sample bags in shipping cartons.

6.4.2 Avoid exposure to excessive elevation or temperature.

6.4.3 Because airborne transport could cause rupture of bags containing toxic samples, only surface shipment is advised.

6.4.4 Deliver bags to laboratory for analysis promptly and in no case later than 24 hours after sampling.

6.5 Analysis. Set the column temperature to 100°C, and the detector temperature to 225°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Use zero-grade helium or 99.999% nitrogen as the carrier gas. Establish a carrier gas flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 mL/min should produce adequate separations.

Observe the base-line periodically and determine that the noise level has stabilized and that baseline drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 mL/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having a retention time corresponding to that of the halogenated organic compound as determined in Section 7.2.1. Measure the halogenated organic compound peak area, A_m with a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary by more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.6 Measure the ambient temperature and barometeric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. STANDARDS, CALIBRATION, AND QUALITY ASSURANCE

7.1 Standards.

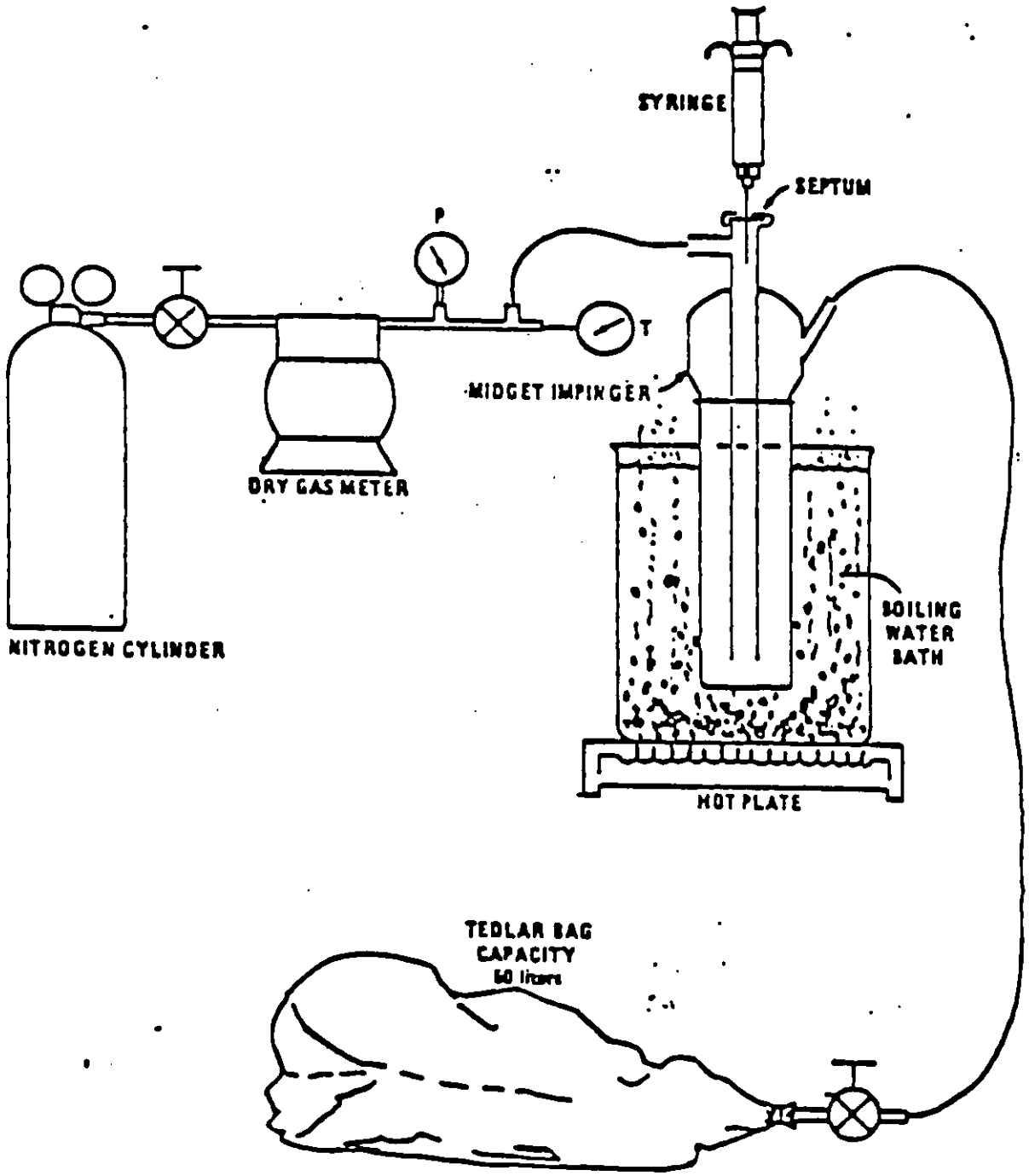
7.1.1 Preparation of Standard Gas Mixtures. (Optional-delete if cylinder standards are used.) Assemble the apparatus shown in Figure 2. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter.

TABLE 1. INJECTION VALUES FOR PREPARATION OF STANDARDS.

Compound	Molecular Weight (M)	Density at 293° A (D)	µl Liquid Required in 50 l N_2 for Approximate Concentration of:		
			200 ppm	100 ppm	50 ppm
Perchloroethylene C_2Cl_4	165.85	1.6230	42.5	21.2	10.6
Trichloroethylene C_2HCl_3	131.40	1.4649	37.3	18.6	9.3
1,1,1-Trichloroethane $C_2H_3Cl_3$	133.42	1.4384	38.6	19.3	9.6
Methylene Chloride CH_2Cl_2	84.94	1.3255	26.6	13.3	6.7
Trichlorotrifluoroethane $C_2Cl_3F_3$	187.38	1.5790	49.3	24.7	12.3
Carbon Tetrachloride CCl_4	153.84	1.5940	40.1	20.1	10.0
Ethylene Dichloride $C_2H_4Cl_2$	98.96	1.2569	32.7	16.4	8.2

Figure 2

TRAIN FOR PREPARATION OF SAMPLES



Refer to Table 1. While the bag is filling, use the 50uL syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200ppm. In a like manner, use the 25uL syringe to prepare bags having approximately 100 and 50 ppm concentrations.

To calculate the specific concentrations, refer to Section 8.1. Tedlar bag gas mixture standards of methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for 1 day; trichloroethylene and 1,1,1-trichloroethene for 2 days; perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. Dibromoethane is subject to decay and analysis would best be carried out within a few hours of sample collection. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Halogenated Organic Compound Retention Time. This section can be performed simultaneously with Section 7.2.2. Establish chromatograph conditions identical with those in Section 6.5, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 6.5), flush the sample loop for 30 seconds at the rate of 100 mL/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the halogenated organic compound peak retention time. Since it is possible that there will be other organics present in the sample, it is very important that positive identification of the halogenated organic compound peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.5. Flush the sampling loop for 30 seconds at the rate of 100 mL/min with one of the standard gas mixtures and activate the sample valve. Record C_c, the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two peak area values versus C_c. When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit.

8. CALCULATIONS

8.1 Optional Standards Concentrations. Calculate each halogenated organic standard concentration prepared in accordance with Section 7.1.1 as follows:

$$C_c = \frac{B \times D}{M \times V_m \times Y} \times \frac{T_m}{293} \times \frac{760}{P_m} \times 24.055 \times 10^3$$

Where:

C_c = Standard concentration in ppm.
B = Volume of gas injected, uL
V_m = Gas volume measured by dry gas meter in liters.
Y = Dry gas meter calibration factor
P_m = Absolute pressure of the dry gas meter, mm Hg.
T_m = Absolute temperature of the dry gas meter, °K.
D = Density of compound at 293 °K.
M = Molecular weight of compound.
10^3 = ug/mg
10^6 = Conversion factor, ppm
24.055 = Volume of 1 ug mole of ideal gas at 293°K and 760 mm Hg, uL/ug-mole

$$24.055 \times 10^3 = \frac{24.055 \times 10^3 \times 10^6}{10^6 \text{ uL/L}}$$

8.2 Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of C_c that corresponds to A_c. Calculate C_s as follows:

$$C_s = \frac{C_c \times P_r \times T_i}{P_i \times T_r \times (1 - S_{wb})}$$

Where:

S_{wb} = The water vapor content of the bag sample, as analyzed.
C_s = The concentration of the halogenated organic in the sample in ppm.
C_c = The concentration of the halogenated organic indicated by the gas chromatograph, in ppm.
P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.
T_i = The sample loop temperature on the absolute scale at the time of analysis, °K.
P_i = The laboratory pressure at time of analysis, mm Hg.
T_r = The reference temperature, the sample loop temperature recorded during calibration, °K.

9. REFERENCES

9.1 Fairheller, W. R.; Kemmer, A.M.; Warner, B. J.; and Douglas, D.Q. "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," EPA Contract No. 68-02-1404, Task 33 and 68-02-2818, Work Assignment 3. January 1978. Revised August, 1978, by EPA.

9.2 Method 23. Proposed to the Code of Federal Register 1980. p.9766

9.3 Bulletin 747. "Separation of Hydrocarbons" 1974. Supelco, Inc. Bellefonte, Pennsylvania 16823.

9.4 Communication from Joseph E. Knoll. Perchloroethylene Analysis by Gas Chromatography. March 8, 1978.

9.5 Communication from Joseph E. Knoll. Test Method for Halogenated Hydrocarbons. December 20, 1978.

9.6 California Air Resources Board, Haagen-Smit Laboratory Division. Procedure for the sampling and analysis of atmospheric C_1 to C_3 halogenated hydrocarbons. CARB Method 103. 1985

9.7 Bradd, Byron B. "Field Validation of EPA Reference Method 23.

APPENDIX J

CARB Method 425

Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

State of California
AIR RESOURCES BOARD

Proposed Method 425

Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources

Adopted (INSERT DATE OF ADOPTION)

PROPOSED METHOD 425
DETERMINATION OF TOTAL CHROMIUM AND HEXAVALENT CHROMIUM EMISSIONS FROM STATIONARY SOURCES

1 APPLICABILITY, PRINCIPLE, AND FIGURES

1. 1 APPLICABILITY

This method applies to the determination of hexavalent chromium (Cr(VI)) and total chromium emissions from stationary sources.

1. 2 PRINCIPLE

Particulate emissions are collected from the source in an alkaline medium by use of CARB METHOD 5. The components of the collected sample are each divided into two equal portions with one portion of each component used for total chromium analysis and the other portion used for hexavalent chromium analysis.

1. 2. 1 Hexavalent Chromium Analysis

For the hexavalent chromium analysis the collected sample component portions are extracted in an alkaline solution and analyzed by the diphenylcarbazide colorimetric method.

1. 2. 2 Total Chromium Analysis

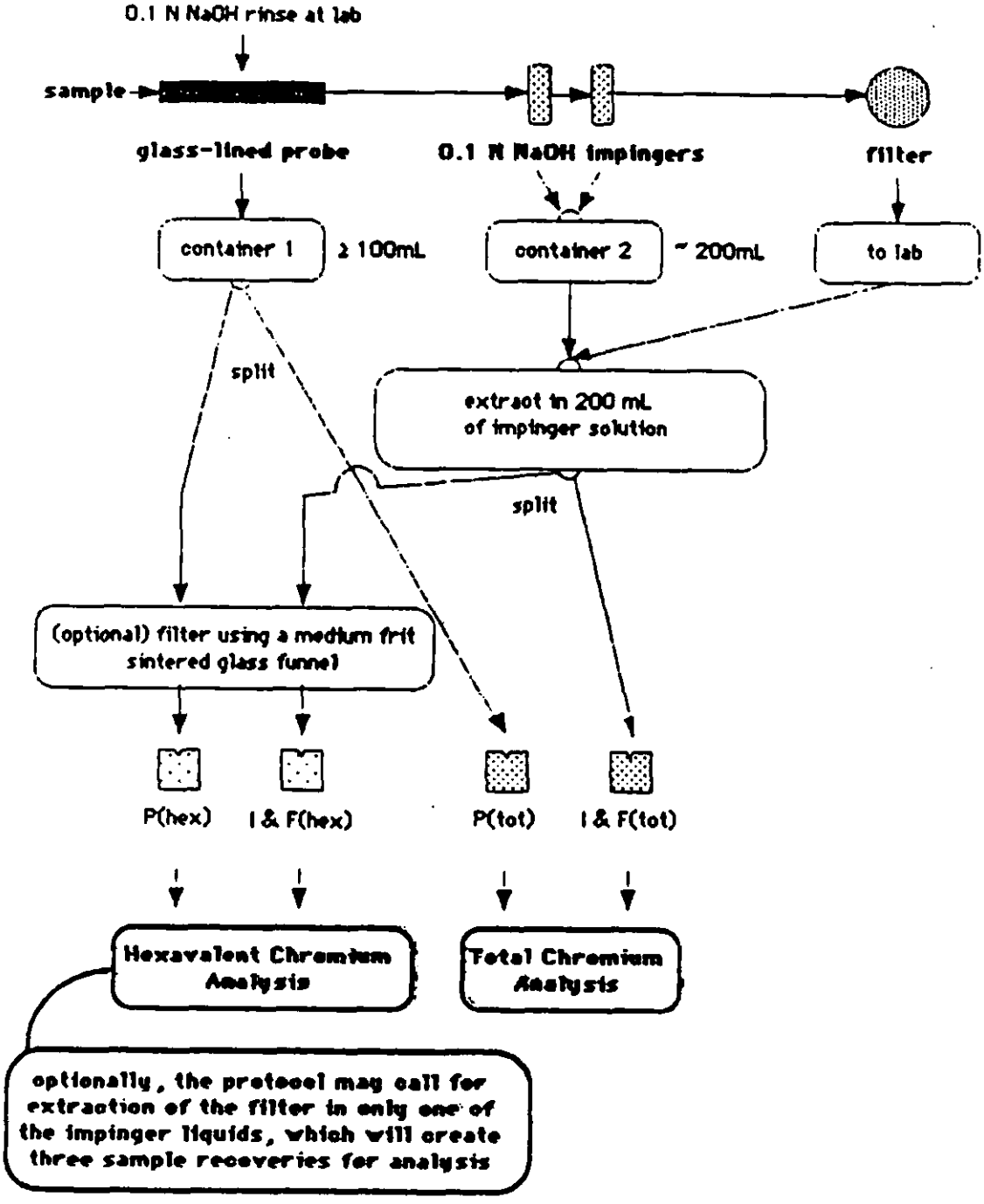
For the total chromium analysis the collected samples must be prepared in order to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. Samples are then subjected to an acid digestion procedure. Following the appropriate dissolution and dilution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the chromium concentration.

1. 3 FIGURES

The following figures summarize features of this method.

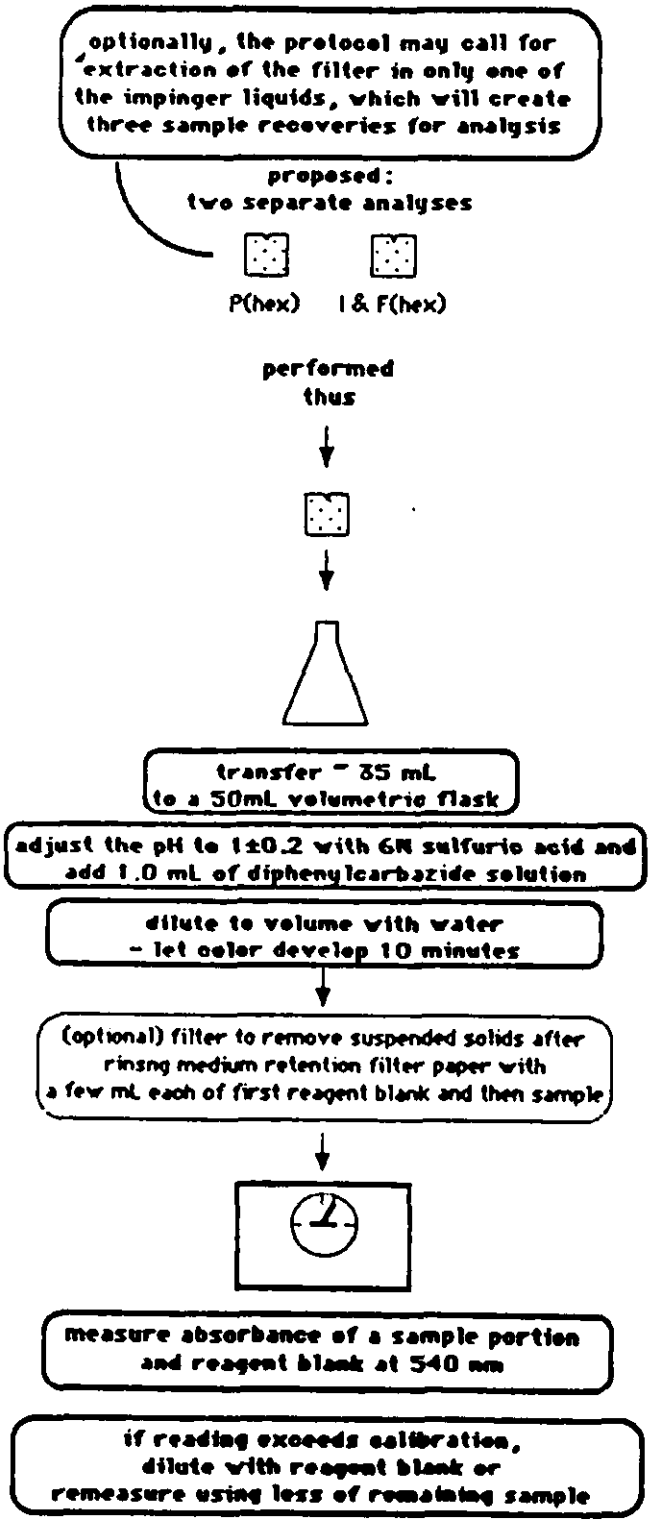
1. 3. 1 Figure 1.

Sample Collection and Recovery for Hexavalent and Total Chromium



1. 3. 2 Figure 2.

Hexavalent Chromium Analysis



2. 4. 2. 2 Nitrogen should not be used as the purge gas because of a possible CN band interference.

2. 4. 2. 3 Low concentrations of calcium may cause interferences; at concentrations above 200 mg/L calcium's effect is constant. Calcium nitrate is therefore added to ensure a known constant effect. This step may be omitted if the sample is known to be free of calcium.

2. 5 ALTERNATIVE METHODS

Total Chromium Determination by Flame Atomic Absorption Spectroscopy

For high total chromium concentrations which are within the detection range of flame atomic absorption spectroscopy, this analytical method may be used instead of the furnace type method specified in these pages.

Other Methods

If other techniques or conditions are used in the analysis of total chromium and/or hexavalent chromium then the tester is required to substantiate the data through an adequate quality assurance program approved by the Executive Officer.

3 APPARATUS

All surfaces which may come in contact with sample must be glass, teflon, or other similarly non-metallic inert material and must be prewashed with detergents, 1+1 HNO_3, and Type II water.

Any other sampling apparatus which, after review by the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

3. 1 SAMPLING TRAIN

Same as CARB Method 5, Section 2.1. except use a glass nozzle, a glass lined stainless steel probe, a Teflon-coated glass fiber filter, and 0.1 N NaOH in the first two impingers.

3. 2 SAMPLE RECOVERY

Same as CARB Method 5, Section 2.2.

3. 3 ANALYSIS

The following apparatus and materials are needed:

3. 3. 1 Analysis of Hexavalent Chromium

3. 3. 1. 1 Philips Beakers

Borosilicate, 125mL, with digestion covers.

3. 3. 1. 2 Filtration Apparatus

Vacuum unit constructed of glass, to accommodate sintered glass funnels.

3. 3. 1. 3 Volumetric Flasks

100-mL and other appropriate volumes.

3. 3. 1. 4 Hot Plate

3. 3. 1. 5 Pipettes

Assorted sizes, as needed.

3. 3. 1. 6 Spectrophotometer

To measure absorbance at 540nm.

3. 3. 2 Analysis of Total Chromium

3. 3. 2. 1 Atomic Absorption Spectrophotometer

Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm and provisions for simultaneous background correction and interfacing with a strip chart recorder.

3. 3. 2. 2 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

3. 3. 2. 3 Graphite Furnace

Any graphite furnace device with the appropriate temperature and timing controls.

3. 3. 2. 4 Strip Chart Recorder

A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4 REAGENTS

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

4. 1 SAMPLING

Same as CARB method 5, Section 3.1, except Teflon-coated glass fiber filters are used, and 0.1 N NaOH is used in the first two impingers. See section 4.3.2 below. Any other sampling method which, after review of the Executive Officer, is deemed equivalent for the purposes of this test method, may be used.

4. 2 SAMPLE RECOVERY

Same as CARB Method 5, Section 3.2.

4. 3 REAGENTS FOR HEXAVALENT CHROMIUM

4. 3. 1 Water

Deionized distilled, meeting American Society for Testing and Materials (ASTM) specification for type reagent - ASTM Test Method D 1193-77. The water should be monitored for impurities.

4. 3. 2 Batch of 0.1% NaOH Solution

The same batch of 0.1N NaOH solution should be used for impinger sampling, sample recovery, preparation, extraction, and analysis. Therefore, sampling and analytical personnel should coordinate their plans so that all steps in sampling and analysis use the same batch of solution which will be prepared fresh for each source test. Typically, dissolve 4.0 g NaOH in water in a 1 liter volumetric flask and dilute to the mark. Repeat, as necessary, so that a single batch of sufficient volume is prepared to serve all of the needs of sampling and analysis. Store the solution in a tightly capped polyethylene bottle.

4. 3. 3 Potassium Dichromate Stock Solution

Dissolve 2.829 g of analytical reagent grade $K_2Cr_2O_7$ in water, and dilute to 1 liter (1 mL = 1000 ug Cr(VI)).

4. 3. 4 Potassium Dichromate Standard Solution

Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 100 ug Hexavalent Chromium) with water.

4. 3. 5 **Sulfuric Acid, 6N**

Dilute 166 mL sulfuric acid to 1000 mL in water.

4. 3. 6 **Diphenylcarbazide Solution**

Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

4. 3. 7 **0.1% Potassium Permanganate Solution**

4. 3. 8 **0.01% Potassium Permanganate Solution**

4. 3. 9 **Removal of Reducing Agents in the Reagents**

The 0.1 N NaOH and the 6N sulfuric acid solutions may contain small amounts of reducing agents that can react with the hexavalent chromium. Potassium permanganate is added to these reagents in order to neutralize these reducing agents. Pipette 3 mL of the extraction solution into cuvettes A and B. Use cuvette A as a sample cell and cuvette B as a reference cell. Zero the instrument at 528 nm with both cuvettes. Wait 10 minutes. Add an adequate amount (uL) of 0.01% potassium permanganate solution to (4.3.9) cuvette A. Enough should be added so that after 10 minutes a slight change in absorbance is observed. This step may have to be repeated a number of times in order to determine the required amount of potassium permangante that is required. From the change in absorbance, calculate the amount of potassium permanganate that is needed to nuetralize the reducing agents found in the reagents. Then pipette the proper volume of higher concentration 0.1% potassium permanganate solution into the reagents. This is done by assuming that the number of milliequivalents of reducing agents in the reagents are equal to the number of milliequivalents of 0.1% potassium permanganate pipetted. This procedure is repeated with the 6N sulfuric acid solution.

4. 4 REAGENTS FOR TOTAL CHROMIUM

4. 4. 1 **ASTM Type II Water (ASTM D1193)**

Refer to section 4.3.1.

4. 4. 2 **Concentrated Nitric Acid**

4. 4. 2. 1 Reagent preparation should use Ultrex or equivalent grade HNO_3.

4. 4. 2. 2 Glassware cleaning should use ACS reagent grade HNO_3.

4. 4. 3 **Hydrogen Peroxide (30%) (Optional)**

4. 4. 4 **Matrix Modifier**

Follow manufacturer's recommendations.

4. 4. 5 **Chromium Standard Stock Solution (1000mg/L)**

Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.829 g of Potassium Dichromate ($K_2Cr_2O_7$, analytical reagent grade) in Type II water and dilute to 1 liter.

4. 4. 6 **Chromium Working Standards**

These chromium standards and the zero standard should be prepared to contain 1.0% (v/v) HNO_3.

5 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5. 1 SAMPLE COLLECTION

All samples are collected from the source by use of CARB Method 5.

5. 2 SAMPLE HANDLING AND PRESERVATION

All surfaces which may come in contact with sample must be glass, teflon, or other similarly non-metallic inert material and must be prewashed with detergents, 1+1 HNO_3, and Type II water.

Contamination Checks

Before use in sampling, to ensure that sampling equipment is clean and free of chromium contamination, apparatus must be cleaned until a sample of final rinse for each probe, impinger, or filter has been analyzed as below the detection limit.

6 PROCEDURES

6. 1 SILICA GEL WEIGHING

For stack gas moisture determination, 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.

separate analyses. Both sample recoveries are split and the hexavalent chromium split is filtered optionally as described above.

6. 3 REAGENT BLANK PREPARATION

Hexavalent Chromium Reagent Blank

For each preparation, transfer 35 mL of solution to a 50mL volumetric flask, adjust the pH to 1.0 ± 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water, and let color develop for 10 minutes.

Total Chromium Reagent Blank

For total chromium, the reagent blank is simply 1 % HNO_3.

6. 4 SAMPLE PREPARATION

6. 4. 1 Hexavalent Chromium Sample Preparation

For each preparation, transfer 35 mL of solution to a 50mL volumetric flask, adjust the pH to 1.0 ± 0.2 with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water, and let color develop for 10 minutes.

6. 4. 2 Total Chromium Sample Preparation

In a beaker, add 10ml of conc. nitric acid to the sample aliquot taken for analysis. Cover the beaker with a digestion cover. Place the beaker on a hot plate and reflux the sample down to 2-3mL. Add another 5mL nitric acid to complete digestion. Reflux the sample volume down to 1mL.

Wash down the beaker walls and digestion cover with distilled water and filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. Adjust the volume to 50 mL or a predetermined value based on the expected metal concentrations. The final concentration of HNO_3 in the solution should be 1 %. The sample is now ready for analysis. The applicability of a sample preparation technique must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

6. 5 ANALYSIS

6. 5. 1 Hexavalent Chromium Analysis

Optionally, the analyst may filter the preparation for clarity at this point. If so, medium retention filter paper should be used. The filter paper should be pre-wetted with a few mL of preparation before filling the absorption cell.

Transfer a portion of the preparation to a 5 cm absorption cell.

Measure the absorbance at the optimum wavelength of 540 nm.

If appropriate, subtract the sample blank absorbance reading to obtain a net reading.

If the absorbance reading of a sample preparation exceeds the calibration range, dilute with reagent blank or re-measure using less of the sample preparation. (There should be about 15mL remaining at this point.)

6. 5. 2 Check for Matrix Effects on the Cr(VI) Results

Since the analysis for Cr(VI) by colorimetry is sensitive to the chemical composition of the sample (matrix effects), the analyst shall check at least one sample from each source using the method of additions as follows: Obtain two equal volume aliquots of the same sample solution. The aliquots should each contain between 6 and 10 ug of Cr(VI) (less if not possible). Spike one of the aliquots with an aliquot of standard solution that contains between 6 and 10 ug of Cr(VI). Now treat both the spiked and unspiked sample aliquots as described in Section 6.4.1 above. Next, calculate the Cr(VI) mass Cs, in ug in the aliquot of the unspiked sample solution by using the following equation:

$$Cs = Ca \frac{As}{At-As} \qquad \text{Eq. 1}$$

where:

Ca = Cr(VI) in the standard solution, ug.

As = Absorbance of the unspiked sample solution.

At = Absorbance of the spiked sample solution.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume. If the results of the method of standard additions procedure used on the single source sample do

not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using this method of standard additions procedure.

6. 5. 3 Total Chromium Analysis

The 357.9-nm wavelength line shall be used.

Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

Inject a measured uL aliquot of preparation into the furnace and atomize. If the concentration found exceeds the calibration range, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

When appropriate, subtract a sample blank reading from a sample reading to obtain a net reading.

7 CALIBRATION, QUALITY CONTROL, AND DATA REPORTING

7. 1 GENERAL

Perform all of the calibrations described in CARB Method 5, Section 5.

7. 2 CALIBRATION AND QUALITY CONTROL FOR HEXAVALENT CHROMIUM

7. 2. 1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The

wavelength scale of the spectrophotometer must read correctly within ±5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 540 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

7. 2. 2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 530 and 550 nm using a 50 ug Cr(VI) standard solution in the sample cell and a reagent blank solution in the reference cell. If a peak does not occur, the spectrophotometer is malfunctioning and should be repaired. When a peak is obtained within the 530 to 550 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the reagent blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum differences in absorbance between the standard and the reagent blank occurs.

7. 2. 3 Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. See section 6.5.2 for the use of the method of standard additions.

7. 2. 4 Each standard for hexavalent chromium is made up fresh in a separate 50mL volumetric flask starting with 35 mL of the same batch of NaOH solution reserved for its sample set. Then an appropriate amount of hexavalent chromium is added to each calibration standard, starting with none for the zero standard. Then 6N sulfuric acid and diphenylcarbazide solution are added in the same manner as in sample preparation.

7. 3 CALIBRATION AND QUALITY CONTROL FOR TOTAL CHROMIUM

7. 3. 1 Either (1) run a series of chromium standards and reagent blanks and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

Calibration standards for total chromium should start with 1% v/v HNO_3 with no chromium for the zero standard with appropriate increases in total chromium concentration in the other calibration standards. The calibration standards should be prepared following the steps outlined in sample preparation.

7. 3. 2 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the standards indicates that the tube should be replaced.

7. 3. 3 Duplicates, spiked samples, and check standards should be routinely analyzed.

7. 3. 4 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

7. 3. 5 Calibration curves must be composed of a minimum of a reagent blank and three total chromium standards. A calibration curve should be made for every batch of samples, unless check standards remain within 10% of the last calibration curve.

7. 3. 6 Dilute samples with reagent blank solution if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

7. 3. 7 Employ a minimum of one matrix-matched sample blank per sample batch to determine if contamination or any memory effects are occurring.

7. 3. 8 Test the system with check standards after approximately every 15 samples.

7. 3. 9 Run one duplicate sample for every 10 samples, providing there is enough sample for duplicate analysis. A duplicate sample is a sample brought through the whole sample preparation.

7. 3.10 Spiked samples or standard reference materials shall be used daily to ensure that correct procedures are being followed and that all equipment is operating properly. This will serve as a check on calibration standards, too.

7. 3.11 Whenever sample matrix problems are suspected, the method of standard additions shall be used for the analysis of all extracts, or whenever a new sample matrix is being analyzed.

7. 3.12 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

7. 3.13 All quality control data should be maintained and available for easy reference or inspection.

7. 4 DATA REPORTING

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

7. 4. 1 Total Cr(VI) in Sample

Calculate and report m_{c6}, the total ug Cr(VI) in the sample. This can be obtained from the calibration curve or from the method of standard additions. Note that m_{c6} is the sum of the masses of hexavalent chromium analyses performed on all sample splits. Also take in account the dilutions when calculating m_{c6}.

Report all sample blank data, too.

7. 4. 2 Total Chromium in the Sample

Calculate and report m_{ct}, the total ug of chromium in the sample. This can be obtained from the calibration curve or from the method of standard additions. Note that m_{ct} is the sum of the masses of total chromium analyses performed on all sample splits. Also take into account the necessary dilutions when calculating out m_{ct}.

Report all sample blank data, too.

7. 4. 3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

Same as Method 5, Section 6.2.

7. 4. 4 **Dry Gas Volume, Volume of Water Vapor, Moisture Content**

Same as Method 5, Sections 6.3, 6.4, and 6.5, respectively.

7. 4. 5 **Cr(VI) Emission Concentration**

Calculate and report $c6_s$ (g/dscm), the Cr(VI) concentration in the stack gas, dry basis, corrected to standard conditions, as follows:

$$c6_s = (10^{-6} g/ug)(m_{c6}/V_{m(std)})$$

7. 4. 6 **Total Chromium Emission Concentration**

Calculate and report ct_s (g/dscm), the total chromium concentration in the stack gas, dry basis, corrected to standard conditions as follows:

$$ct_s = (10^{-6} g/ug)(m_{ct}/V_{m(std)})$$

7. 4. 7 **Isokinetic Variation, Acceptable Results**

Same as Method 5, Sections 6.11 and 6.12, respectively.

8 REFERENCES

8. 1 US. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, "SW-846 (1980), SW-846 Revision A (August 8, 1980), and SW-846 Revision B (July 1981).

8. 2 Cox, X.B., R.W., R.W. Linton, and F.E. Butler. Determination of Chromium Speciation in Environmental Particles- A Multitechnique Study of Ferrochrome Smelter Dust. Accepted for publication in Environmental Science and Technology.

8. 3 Same as in Bibliography of Method 5, Citations 2 to 6 and 7.

8. 4 California Air Resources Board, Inorganic Analysis Section. (1988)

APPENDIX E

CARB Method 15

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

APPENDIX E

HYDROGEN SULFIDE

Determination of hydrogen sulfide emissions is based upon a modification of CARB Method 15.

In this modification a sample of the exhaust gas is collected in a tedlar bag following the test method detailed in CARB Method 410A, included in Appendix G of this volume. Analysis of the hydrogen sulfide in the bag is conducted using the GC/FPD analytical method detailed in CARB Method 15.

A sample holding time of not more than three (3) days has been determined by the analytical laboratory.

State of California
Air Resources Board

Method 15

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

Adopted: June 29, 1983

METHOD 15 - DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES

INTRODUCTION

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

1. Principle and Applicability

1.1 Principle: A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) by gas chromatographic (GC) separation and flame photometric detection (FPD).

1.2 Applicability: This method is applicable for determination of the above sulfur compounds from tail gas control units of sulfur recovery plants.

diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of Section 4.1.

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

4. Precision

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

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ± 5 percent.

5. Apparatus

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

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

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

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

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1°C.

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

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

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

5.3.4 Flame Photometric Detector.

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

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

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

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

To demonstrate that adequate resolution has been achieved the tester must submit a chromatograph of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of fullscale. Base line separation is defined as a return to zero ± 5 percent in

the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Control Agency's Authorized Representative.

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

5.5.2 Flow System. To measure air flow over permeation tubes at ± 2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within $\pm 0.1^{\circ}C$.

5.5.4 Temperature Gauge. Thermometer of equivalent to monitor bath temperature within $\pm 1^{\circ}C$.

6. Reagents

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

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, COS, and CS_2, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. Pretest Procedures

The following procedures are helpful in preventing any problem which might occur later and invalidate the entire test.

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

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

Equation 3-1

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

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

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

Equation 3-2

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

7.1 After the complete measurement system has been set up at the site the following procedures are to be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or the of GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component

or the completed system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within $\pm 0.1^{\circ}C$. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

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

Equation 15-1

where

C = Concentration of permeant produced in ppm.

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

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

L = Flow rate, l/min, of air over permeant @ $20^{\circ}C$, 760 mm Hg.

K = Gas constant at $20^{\circ}C$ and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of Analysis System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H_2S (developed under 8.3) determine the

diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three more more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of section 4.1 are still applicable.

9. Sampling and Analysis Procedure

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

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

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

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. Post-Test Procedures

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling

losses of 0-20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in secton 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

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

concentrations may be calculated using the equation for the least squares line.

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

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

Equation 15-2

where:

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

H_2S = Hydrogen sulfide, ppm.

COS = Carbonyl sulfide, ppm.

CS_2 = Carbon disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average SO_2 equivalent will be determined as follows:

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

Equation 15-3

where:

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

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

N = Number of analyses performed.

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

12 Example System

12.1 Apparatus

12.1.1 Sample System

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

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

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

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

made of inert materials. The dilution system which is heated to 120°C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

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

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

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

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

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

12.1.3 Gas Chromatrograph.

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

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

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

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

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

12.1.3.6 Detector. Flame photometric detector.

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

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

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

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

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

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

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of $30^{o}C$ within $\pm$ $0.1^{o}C$.

12.2 Reagents.

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

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

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

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

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at $30.0^{o}C$.

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

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

13. Bibliography

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

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

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

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

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

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

APPENDIX F

CARB Method 101A

Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators

State of California
Air Resources Board

Method 101A

Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators

Adopted: March 28, 1986

INTRODUCTION

This method is similar to Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for collection.

1. Applicability and Principle

1.1 Applicability — This method applies to the determination of particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations.

1.2 Principle: — Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. Range and Sensitivity

2.1 Range. After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 Sensitivity The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3. Interfering Agents

3.1 Sampling. Excessive oxidizable organic matter in the stack gas prematurely depletes the $KMnO_4$ solution and thereby prevents further collection of Hg.

3.2 Analysis. Condensation of water vapor on the optical cell windows causes a positive interference.

4. Precision

Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 ug Hg/ml in the concentration range of 50 to 130 ug Hg/m^3.

5. Apparatus

5.1 Sampling Train and Sample Recovery.

Same as Method 101, Sections 5.1 and 5.2 respectively, except for the following variations:

5.1.1 Probe Liner.

Same as Method 101, Section 5.1.2 except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 Filter Holder (Optional). Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 15° C (248 ± 25° F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 Analysis. The apparatus needed for analysis is the same as Method 101, Sections 5.3 and 5.4, except as follows:

5.2.1 Volumetric Pipetts.

Class A: 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

5.2.2 Graduated Cylinder.

25-ml

5.2.3 Steam Bath.

6. Reagents Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 Sampling and Recovery

The reagents used in sampling and recovery are as follows:

6.1.1 Water

Deionized distilled, meeting ASTM Specifications for Type I Reagent Water - ASTM Test Method D1193-77 (incorporated by reference - see (61.18). If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizables.

6.1.2 Nitric Acid (HNO_3). 50 Percent (V/V).

Mix equal volumes of concentrated HNO and deionized distilled water, being careful to slowly add the acid to the water.

6.1.3 Silica Gel.

Indicating type, 6- to 16- mesh. If previously used, dry at 175° C (350° F) for 2 hr. The tester may use new silica gel as received.

6.1.4 Filter (Optional).

Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 um dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.

6.1.5 Sulfuric Acid (H_2SO_4). 10 Percent (V/V). Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.

6.1.6 Absorbing Solution. 4 Percent $KMnO_4$ (W/V). Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

6.2 Analysis. The reagents needed for analysis are listed below:

6.2.1 Tin (II) Solution.
Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 ug of tin (II) chloride [or 25 g if tin (II) sulfate] crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4 or other strong acids for the HCl.

6.2.2 Sodium Chloride - Hydroxylamine Solution. Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in deionized distilled water and dilute to 100 ml.

6.2.3 Hydrochloric Acid (HCl). 8 N.

Dilute 67 ml of concentrated HNO_3 to 100 ml with deionized distilled water (slowly add the HCl to the water).

6.2.4 Nitric Acid, 15 Percent (V/V).

Dilute 15 ml of concentrated HNO_3 to 100 ml with deionized distilled water.

6.2.5 Mercury Stock Solution. 1 mg Hg/ml.

Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g mercury (II) chloride in 75 ml of deionized distilled water. Add 100 ml of concentrated HNO and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 Intermediate Mercury Standard Solution. 10 ug Hg/ml.

Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (Section 6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO_3 solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.7 Working Mercury Standard Solution. 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (Section 6.2.6) into a 250-ml volumetric flask. Add 5 ml of 4 percent $KMnO_4$, absorbing solution and 5 ml of 15 percent HNO_3. Adjust the volume to exactly 250 ml with deionized distilled water. Mix thoroughly.

6.2.8 Potassium Permanganate. 5 Percent (W/V). Dissolve 5 ug of $KMnO_4$ in deionized distilled water and dilute to 100 ml.

6.2.9 Filter

Whatman No. 40 or equivalent.

7. Procedure.

7.1 Sampling. The sampling procedure is the same as Method 101, except for changes due to the use of $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 Preliminary Determinations.

The preliminary determinations are the same as those given in Method 101, Section 7.1.2, except for the absorbing solution depletion sign. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted. In cases where an excess of water condensation is encountered, collect two runs to make one sample.

7.1.2 Preparation of Sampling Train.

The preparation of the sampling train is the same as that given in Method 101. Section 7.1.3, except for the cleaning of the glassware [probe, filter holder (if used) impingers, and connectors] and the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3 tap water, 8 N HCl tap water, and finally deionized distilled water. Then place 50 ml of 4 percent $KMnO_4$ in the first impinger and 100 ml in each of the second and third impingers.

If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter and place the

gasket in proper position to prevent the sample gas stream from by-passing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3 Sampling Train Operation. In addition to the procedure given in Method 101, Section 7.1.5 , maintain a temperature around the filter (if applicable) of 120 ± 14(-GL-)° C (248° ± 25° F).

7.2 Sample Recovery Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid out from the impingers.

Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe, impinger assembly, and (if applicable) filter assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 Container No. 1. (Impinger, Probe, and Filter Holder). Use a graduated cylinder, measure the liquid in the first three impingers to within ± 1 ml. Record the volume of liquid present (e.g., see Figure 5-3 of Method 5 in Part 60 of 40 CFR). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 7.1.2) Place the contents of the first three impingers into a 1000-ml glass sample bottle. (Note. - If a filter is used, remove the folter from its holder, as outlined under "Container No. 3" below.) Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner and front half of the filter holder (if applicable) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent $KMnO_4$, solution: add all washings to the 1000-ml glass sample bottle; remove any

residual brown deposits on the glassware using the minimum amount of 8 N HCl required; and add this HCl rinse to this sample container.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

7.2.2 Container No. 2. (Silica Gel) Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the

gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g: record this weight.

7.2.3 Container No. 3 (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100 ml glass sample bottle, and add 20 to 40 ml of 4 percent $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-ml sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

7.2.4 Container No. 4 (Filter Blank). If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 Container No. 5. (Absorbing Solution Blank) For a blank place 500 ml of 4 percent $KMnO_4$, absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 Sample Preparation. Check liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below.

7.3.1 Containers No. 3 and No 4. (Filter and Filter Blank). If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers and heat the beakers on a steam bath until most of the liquid has

evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70° C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 Container No 1 (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman No. 40 filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4 percent $KMnO_4$, absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.3.3 Container No. 5 (Absorbing Solution Blank). Treat this container as described in Section 7.3.2. Combine this filtrate with the filtrate with Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 Analysis. Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 to 8.4. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within ± 3 percent of their average value. If the 10-ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

8. Calibration and Standards

The calibration and standards are the same as Method 101, Section 8, except for the following variations:

8.1 Optical Cell Heating System Calibration. Same as method 101, Section 8.2 except use a 25 ml graduated cylinder to add 25 ml of deionized distilled water to the bottle section of the aeration cell

8.2 Spectrophotometer and Recorder Calibration

The mercury response may be measured by either peak height or peak area. (Note: The temperature of the solution affects the rate at which elemental Hg is released from a solution, and consequently, it

affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.) Set the spectrophotometer wave length at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condenstation.

Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell. (Note: Always add the Hg-containing solution to the aeration cell after the 25 ml of deionized distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent $KMnO_4$, absorbing solution followed by 5 ml of 15 percent HNO_3, and 5 ml of 5 percent KMnO4, to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride hydroxylamine in 1-ml increments until the solution is colorless. Now add 5 ml of tin (II) solution to the aeration bottle through the side arm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

9. Calculations

9.1 Dry Gas Volume, Volume of Water Vapor and Moisture Content, Stack Gas Velocity, Isokinetic Variation and Acceptable Results and Determination of Compliance.

Same as Method 101. Section 9.1, 9.2, 9.3, 9.8 and 9.7 respectively, except use data obtained

9.2 Total Mercury

For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within $\pm$ 3 percent of their average for the contribution of the field blank. Then calculate the total Hg content in ug in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 Mercury Emission Rate

Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-1. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K\ m_{Hg}\ V_s\ A_s\ (86{,}400 \times 10^{-6})}{[V_m\ (std.)] + V_w\ (std.)](T_s/P_s)} \qquad \text{Equation 101A-1}$$

Where:

m_{Hg} = Total Hg content in each sample ug.

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

A_s = Stack cross-sectional area m^2 (ft).

86,400 = Conversion factor, sec/day.

10^{-6} = Conversion factor, g/ ug.

V_m (Std) = Dry gas sample volume at standard conditions corrected for leakage (if any), m^3 (ft^3).

V_w(std) = Volume of water vapor at standard conditions, m^3 (ft^3).

T = Absolute average stack gas temperature °K (°R).

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

K = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in Hg for English units

10. Bibliography

1. Same as Method 1101, Section 10

2. Mitchell, W.J., M.R. Midgett, J.C. Suggs, and D. Albrinck Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, Publication No. EPA-600/4-79-058. September 1979

APPENDIX K

CARB Method 426

Determination of Cyanide
Emissions from Stationary Sources

HYDROGEN CYANIDE

Hydrogen Cyanide emissions from the source were determined using a modification of CARB Method 426.

In this modification, particulate cyanides were collected in the probe wash and pre-impinger filter, and were discarded. All gaseous cyanides collected in the impinger section of the sample train were analyzed using the analytical protocol detailed in Method 426, and were reported as hydrogen cyanide.

State of California
Air Resources Board

Method 426

Determination Of Cyanide Emissions From Stationary Sources

Adopted: January 22, 1987

Method 426 - Determination of Cyanide Emissions From Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method is for determination of cyanides in aerosol and gas emissions from stationary sources. Cyanide is defined as cyanide ion and complex cyanide converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

1.2 Principle

Particulate and gaseous emissions are extracted isokinetically from the stack and passed through an impinger-filter train where the cyanide is collected on a glass-fiber filter and in a solution of sodium hydroxide. The combined filter extract and impinger solution are analyzed for cyanide by either titrating with standard silver nitrate in the presence of a silver sensitive indicator or by a colorimetric procedure using Chloramine-T with either pyridine-barbituric acid or pyridine-pyrazolone color forming reagents.

2. RANGE AND SENSITIVITY

The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide greater than 1 mg/L (0.25 mg/250 mL of absorbing liquid). The detection limit for this procedure is 0.3 mg/L.
The colorimetric procedure has an optimum working range of 0.02 - 1 mg/L, and a detection limit of 0.01 mg/L.

3. INTERFERENCES

Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the procedure described in Section 6.3.3.2. The apparatus for this procedure is shown in Figure 3.

Positive errors may occur with samples that contain nitrite and/or nitrate. During the distillation, nitrite and nitrate form nitrous acid which reacts with some organic compounds to form oximes. These compounds will decompose under test conditions to generate HCN. The interference of nitrite and nitrate is eliminated by pretreatment with sulfamic acid.

Since oxidizing agents may decompose most of the

cyanides, they must be removed during sample recovery (Section 6.2.1.1).
If the analytical method herein recommended does not give the desired sensitivity in the presence of interfering substances in the sample, the tester may select an equivalent procedure, subject to the approval of the Executive Officer. The tester must then produce data to demonstrate that the method is equivalent, and substantiate this data through an adequate quality assurance program approved by the Executive Officer.

4. APPARATUS

The following sampling apparatus is recommended. The tester may use an alternative sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of the method.

4.1 Sampling Train

A schematic diagram of the sampling train is shown in Figure 1. This is similar to the CARB Method 5 sampling train with some minor changes which are described below.

4.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer and Gas Density Determination Equipment. Same as Method 5 Sections 2.1.1 to 2.1.6, and 2.1.8 to 2.1.10, respectively.

4.1.2 Impingers. Four impingers are connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design modified by replacing the tip with a 1-cm (0.5 in.) I.D. glass tube extending to 1 cm from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.
The first and second impingers shall contain known quantities of 0.1 N NaOH (Section 6.1.3). The third shall be empty, and the fourth shall contain a known weight of silica gel or equivalent desiccant.
In the case of sources which produce significant levels of carbon dioxide, the tester may substitute sodium bicarbonate for sodium hydroxide in the first and second impingers.
A thermometer which measures temperatures to within 1°C (2°F), should be placed at the outlet of the fourth impinger.

4.2 Sample Recovery.

The following items are needed:

4.2.1 Probe Liner and Probe Nozzle Brushes, Petri Dishes, Plastic Storage Containers, Rubber Policeman and Funnel. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.6, and 2.2.7, respectively.

4.2.2 Wash Bottles. Glass (2)

4.2.3 Sample Storage Containers. Alkali resistant polyethylene bottles. Impinger and probe solutions and washes, 1000 mL. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to attack by alkali.

4.2.4 Graduated Cylinder and/or Balance. To measure the volume of condensed water to within 2 mL, or the weight to within 1 g. Use a graduated cylinder that has a minimum capacity of 500 mL, and subdivisions no greater than 2 mL. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less).

4.2.5 Funnel. Glass, to aid in sample recovery.

4.3 Analysis. The following equipment is needed:

4.3.1 Reflux distillation apparatus assembled as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

4.3.2 Microburet, 5.0 mL (for titration).

4.3.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

4.3.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask should be of 1-liter size with inlet tube and provision for condenser as in 4.3.1. The sulfide scrubber may be a Wheaton Bubbler #709682 with 29/42 joints, size 100 mL. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube of this absorber should be fritted.

4.3.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

4.3.6 Erlenmeyer Flasks. 125 mL. 24/40 T.

4.3.7 Whatman No. 42 filter paper (or equivalent).

4.3.8 Volumetric Flasks. 100-mL, 250-mL, and 1000-mL.

4.3.9 Balance - Analytical. Capable of accurately weighing to the nearest 0.0001 g.

5. REAGENTS

Unless otherwise specified, use ACS reagent grade chemicals or equivalent.
Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board.

5.1 Sampling. The following reagents are needed:

5.1.1 Glass Fiber Filters, Silica Gel, Crushed Ice and Stopcock Grease. Same as Method 5, Sections 3.1.1, 3.1.2, 3.1.4 and 3.1.5, respectively.

5.1.2 Water. Deionized, distilled, to conform to ASTM Specification D1193-77, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

5.1.3 Sodium Hydroxide solution, 0.1 N. Dissolve 4.0 g NaOH in deionized distilled water, and dilute to 1 liter with water.

5.2 Sample Recovery.

5.2.1 Sodium Hydroxide solution, 0.1 N. Same as 5.1.3 above.

5.2.2 Sodium Hydroxide solution, 10 N. Dissolve 40 g NaOH in deionized distilled water, and dilute to 100 mL.

5.2.3 Ascorbic acid, crystals.

5.2.4 Potassium iodide-starch test paper (KI-starch paper).

5.3 Analysis. The following reagents are needed:

5.3.1 Water. Same as 5.1.2 above.

5.3.2 Sodium Hydroxide Solution, 1.25 N. Dissolve 50 g of NaOH in deionized distilled water, and dilute to 1 liter.

5.3.3 Dilute Sodium Hydroxide Solution, 0.25 N. Dilute 200 mL of 1.25 N sodium hydroxide solution (5.3.2) to 1000 mL with deionized distilled water.

5.3.4 Sulfuric acid, 18 N. Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of deionized distilled water.

5.3.5 Sodium dihydrogenphosphate, 1 M. Dissolve 138 g of $NaH_2PO_4.H_2O$ in 1 liter of deionized distilled water. Refrigerate this solution.

5.3.6 Standard silver nitrate solution, 0.0192 N. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in deionized distilled water, and dilute to 1000 mL (1 mL = 1 mg CN^-).

5.3.7 Stock Cyanide Solution. Dissolve 2.51 g of KCN and 2 g of KOH in 900 mL of deionized distilled water. Standardize with 0.0192 N $AgNO_3$ (Section 5.3.6). Dilute to appropriate concentration so that 1 mL = 1 mg CN^-.

5.3.8 Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution (1 mL = 1 mg CN^-) to 1000 ml with deionized distilled water. (1 mL = 100.0 ug CN^-).

5.3.9 Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle (1 mL = 10.0 ug CN^-).

5.3.10 Cyanide Calibration Standards. Pipet 0.0, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 mL of the working cyanide standard solution (5.3.9) into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25 N sodium hydroxide, and dilute to 250-mL with deionized distilled water. These working standards contain 0.0, 0.04, 0.08, 0.20, 0.40, 0.60, and 0.80 mg CN^-/L, respectively. Prepare as needed, additional standards at other concentrations in a similar manner.

5.3.11 Rhodanine indicator. Dissolve 20 mg of p-dimethyl amino-benzalrhodanine in 100 mL of acetone.

5.3.12 Chloramine-T solution. Dissolve 1.0 g of white, water-soluble Chloramine-T in 100 mL of deionized distilled water and refrigerate until ready to use. Prepare fresh daily.

5.3.13 Color reagent - One of the following may be used:

5.3.13.1 Pyridine-Barbituric Acid Reagent. Place 15 g of barbituric acid in a 250 mL

volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of conc. HCl, mix, and cool to room temperature. Dilute to 250 mL with deionized, distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.13.2 Pyridine-pyrazolone solution.

(a) 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, and heat to 60°C with stirring. Cool to room temperature.

NOTE: It is imperative that this synthesis be performed as directed.

(b) 3,3'Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

(c) Pour solution (5.3.13.2a) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (5.3.13.2b) collecting the filtrate in the same container as filtrate from (5.3.13.2a). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

5.3.14 Magnesium chloride solution. Weigh 510 g of $MgCl_2.6H_2O$ into a 1000 mL flask. Dissolve and dilute to 1 liter with deionized distilled water.

5.3.15 Lead acetate. Dissolve 30 g of $Pb(C_2H_3O_2).3H_2O$ in 950 mL of deionized distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.

5.3.16 Sulfamic acid.

6. PROCEDURE

6.1 Sampling.

Because of the complexity of this method, testers should be trained and experienced with the test procedures in

order to ensure reliable results.

6.1.1 Pretest Preparation. Follow the same general procedure described in Method 5, Section 4.1.1, except the filter need not be weighed.

6.1.2 Preliminary Determinations. Follow the same general procedure described in Method 5, Section 4.1.2.

6.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 mL of 0.1 N NaOH 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. Assemble the train as shown in CARB Method 5, Figure 5-1.

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

6.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in CARB Method 5, Figure 5-2.

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

6.2 Sample Recovery.

Begin proper clean-up procedure as soon as the probe is removed from the stack at the end of the sampling period.

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

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the glassware inlet where the probe was fastened and cap the inlet. Remove the umbilical cord from the last impinger and cap

the impinger. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to a cleanup area, which is clean and protected from the wind so that the chances of contaminating or losing the sample are minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions.
Check the pH of the impinger solutions to ascertain that the pH is still basic, and that the test was a valid one.

Treat the samples as follows:

6.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in a glass sample container containing 50 mL of 0.1 N NaOH. Carefully transfer any visible particulate matter and/or filter fibers that adhere to the filter holder gasket with a dry Nylon bristle brush and/or sharp-edged blade.

6.2.1.1 Oxidising agents. If oxidising agents are known or suspected to be present, test and treat the sample as follows. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper). A blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.2.1.2 Preservation. Samples must be preserved with 2 mL 10 N sodium hydroxide (5.3.2) per liter of sample (pH $\geq$ 12) at the time of collection.

6.2.2 Container No. 2 (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces that have been exposed to the sample (including the probe nozzle, probe fitting, probe liner, and front half of the filter holder) with 0.1 N NaOH. Place the wash in a glass sample storage container. Measure and record (to the nearest 2-mL) the total amount of 0.1 N NaOH used for each rinse. Perform the rinses with 0.1 N NaOH as follows:

Carefully remove the probe nozzle and rinse the

inside surface with 0.1 N NaOH from a wash bottle. Brush with a Nylon-bristle brush, and rinse until the rinse shows no visible particles, after which, make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with 0.1 N NaOH in a like manner until no visible particles remain.

Rinse the probe liner with 0.1 N NaOH. While squirting the sodium hydroxide rinse into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with the 0.1 N NaOH. Let the 0.1 N NaOH drain from the lower end into the sample container. The tester may use a glass funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt 0.1 N NaOH into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any liquid and particulate matter brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N NaOH and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with 0.1 N NaOH and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above. It is recommended that two people clean the probe to minimize loss of sample: Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, brush and rinse with 0.1 N NaOH the inside of the front half of the filter holder. Brush and rinse each surface three times or more, if needed, to remove visible particulate matter. Make a final rinse of the brush and filter holder.

After all washings have been collected in the sample container, test a drop of the sample with potassium iodide-starch test paper (KI-starch paper). A blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on

the indicator paper. Then add an additional 0.6 g of ascorbic acid for each litre of sample volume.

Samples must be preserved with 2 mL 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.

Tighten the lid on the sample container so that the fluid will not leak out when it is transported to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during shipment. Label the container to clearly identify its contents.

Rinse the glassware a final time with water to remove residual NaOH before reassembling. Do not save the final rinse water.
Repeat the test for oxidising agents (6.2.1.1) and then preserve the sample (6.2.1.2).

6.2.3 Container No. 3 (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent, and note its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel and rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the procedure for Container No. 2 under Section 6.4 (Analysis).

6.2.4 Container No. 4 (Impingers). If the volume of liquid is large, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease and cap the joints.

2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

3. Transfer the contents of the impingers to a 500-mL graduated cylinder. Remove the outlet ball joint cap and drain the contents through this opening. Do not separate the impinger

parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within ±2mL. Alternatively, determine the weight of the liquid to within ±0.5 g. Record in the log the volume or weight of the liquid present, and the occurrence of any color or film in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).
Determine the pH of the impinger solution to ascertain whether it is still basic and whether the test was a valid one.

4. Transfer the contents to Container No. 4.

5. Note: In steps 5 and 6 below, measure and record the total amount of 0.1 N NaOH used for rinsing. Pour approximately 30 mL of 0.1 N NaOH into each of the first three impingers and agitate the impingers. Drain the 0.1 N NaOH through the outlet arm of each impinger into Container No. 3. Repeat this operation a second time; inspect the impingers for any abnormal conditons.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N NaOH; transfer this rinse into Container No. 3. (Do not rinse or brush the glass-fritted filter support). Repeat the procedure described in Section 6.2.1.1 above.

   Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

6.2.5 Sample Blanks (Container No.5). Prepare a blank by placing an unused filter in a glass container, and adding a volume of recovery solution identical to the total volume in Containers No. 1, 2, and 4. Process the blank in the same manner as the sample.

6.3 Sample Preparation.

6.3.1 Container No. 1 (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-mL Erlenmeyer flask. Rinse the petri dish with 10 mL of 1.25 N NaOH to insure a quantitative transfer and add to the

flask. Pipet 25 mL of 1.25 N NaOH into the flask. Cap the flask, place on a shaker and shake for at least 30 minutes at moderate speed to complete the extraction.

6.3.2 Containers No. 2 and No. 4 (Probe and Impingers). Check the liquid level in Containers No. 2 and/or No. 4 to determine whether any sample was lost during shipment. Record observations on the analysis sheet. If a noticeable amount of leakage has occurred, either void the sample or take steps, subject to approval by the Executive Officer, to adjust the final results. Combine the contents of Containers No. 2 and No. 4 with the filter extract (6.3.1) for analysis.

6.3.3 Distillation procedure.

6.3.3.1 Samples without sulfide.
Place 500 mL of the combined sample (Section 6.3.2) or an aliquot diluted to 500 mL in the 1 liter boiling flask. Pipet 50 mL of 1.25 N sodium hydroxide (5.3.2) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap as shown in Figure 1 or Figure 2.

Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the inlet tube. Proceed to Section 6.3.5.

6.3.3.2 Samples that contain sulfide.
Place 500 mL of the combined sample (6.3.2) or an aliquot diluted to 500 mL in the 1-liter boiling flask. Pipet 50 mL of 1.25 N sodium hydroxide into the absorbing tube. Add 25 mL of lead acetate solution (5.3.15) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber as shown in Figure 3. The flow meter is connected to the outlet tube of the cyanide absorber.

Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enter the boiling flask through the air

inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 6.3.5.

6.3.4 If samples contain NO_3^- and or NO_2^-, add 2 g of sulfamic acid (5.3.16) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

6.3.5 Slowly add 50 mL 18 N sulfuric acid (5.3.4) through the air inlet tube. Rinse the tube with deionized distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (5.3.13) into the air inlet and wash down with a stream of water.

Heat the solution to boiling. Reflux for one hour. Turn off the heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with deionized distilled water, and add the washings to the flask. Dilute to volume with deionized distilled water.

6.3.6 Sample Blank (Container No. 5). Treat in the same manner as the sample (Sections 6.3.3 to 6.3.5). Use the absorbance obtained for the blank to correct the sample measurement.

6.4 Analysis.

6.4.1 Colorimetric Procedure
Sample (Containers No.1, No. 2, and No. 4.). Withdraw 50 mL or less of the solution from the 250-mL volumetric flask (Section 6.3.3.1 or 6.3.3.2) and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (5.3.3). Add 15.0 mL of 1 M Sodium dihydrogenphosphate solution (5.3.5) and mix.

6.4.1.1 Pyridine-Barbituric Acid Method. Add 0.5 mL of chloramine T (5.3.12) and mix. See Notes 1 and 2. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (5.3.13.1) and mix. Dilute to volume with distilled water and mix again. Allow 8 minutes

for color development then measure the absorbance at 578 nm in a 1 cm cell within 15 minutes. Read ug CN^-/50ml from the calibration curve obtained in Section 7.2. If the absorbance does not fall within the range of the calibration curve, repeat the procedure using a smaller aliquot.

6.4.1.2 Pyridine-pyrazolone method. Add 0.5 mL of chloramine T (5.3.12) and mix. See Notes 1 and 2. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (5.3.13.2) and mix. Dilute to volume with distilled water and mix again. After 40 minutes, measure the absorbance at 620 nm in a 1 cm cell. Read the concentration of the sample (ug CN^-/50 mL) from the calibration curve obtained in Section 7.2. If the absorbance of the sample does not fall within the range of the calibration curve, repeat the analysis using a smaller aliquot.

NOTE 1 Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 mL of chloramine T. After one minute, recheck the sample.

NOTE 2 If more than 0.5 mL of Chloramine T is used with the pyridine-pyrazolone color reagent, this will prevent the color from developing.
If more than 0.5 mL of Chloramine T is used with the pyridine-barbituric acid color reagent, this will accelerate the rate at which the color fades.

6.4.2 Titration Procedure.
If the sample contains more than 1 mg of CN^-/L, transfer the distillate (6.3.3), or a suitable aliquot diluted to 250 mL, to a 500-mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator. Titrate with standard silver nitrate solution (5.3.6) to the first change in color from yellowish brown to pink. Titrate the blanks using the same amount of sodium hydroxide and indicator as in the sample.

The analyst should familiarize himself with the end point of the titration and the amount of

indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be used to obtain a more precise titration.

6.4.3 Sample Blank (Container No.5). Follow the same procedure used for the sample (Section 6.4.1 or 6.4.2 above). Use the same aliquot size as that used for the sample.

6.4.4 Container No. 3 (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7. CALIBRATION.

7.1 Sampling Train Calibration. Calibrate the sampling train components according to the following sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

7.2 Spectrophotometer. Pipet 50 mL of each calibration standard (5.3.10) into a 100-mL volumetric flask, and treat according to Section 6.4.1. These standards will contain 0.0, 2.0, 4.0, 10.0, 20.0, 30.0, and 40.0 ug CN^-/50mL.

With the spectrophotometer at 620 nm for pyridine-pyrazolone, or 578 nm for pyridine-barbituric acid, use the reagent blank (7.2) to set the absorbance to zero. Determine the absorbance of the standards, and plot net absorbance versus ug CN^-/50 mL. Draw a smooth curve through the points. The curve should pass through the origin.

7.2.1 Samples without sulfide.
It is not imperative that all standards be distilled in the same manner as the samples. However, it is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

7.2.2 Samples that contain sulfide.
It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increrases, the recovery

decreases. It is recommended that at least 3 standards be distilled.

7.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (5.3.8) or the working standard (5.3.9) to 500 ml of sample to insure a level of 20 ug/L. Proceed with the analysis as in Section 6.3.3.

8. CALCULATIONS.

8.1 Nomenclature

A_t = Aliquot of total sample added to the still, mL (6.3.3)

A_d = Aliquot of distillate taken for color development, mL (6.4.1).

C_c = ug CN^- from the calibration curve

V_d = Volume of distillate after dilution, mL (6.3.3)

V_t = Total volume of cyanide sample after final dilution, mL (6.3.2)

m_t = Total cyanide in sample, mg

C_s = Concentration of cyanide in the stack gas, mg/m^3, dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293 ^oK (528^oR).

Q_t = Aliquot of sample used for titration, mL

T = Volume of $AgNO_3$ for titration of sample, mL

B = Volume of $AgNO_3$ for titration of blank, mL

8.2 Dry Gas Volume.
Using the data from this test, calculate $V_{m(std)}$ the total volume of dry gas metered corrected to standard conditons (20^oC and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{m(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

8.3 Volume of Water Vapor and Moisture content.
Using data obtained in this test and Equations 5-2 and 5-3 of Method 5, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas.

8.4 Total Cyanide in Sample.

Colorimetric Procedure. Use the following equation to calculate the amount of CN^- in the sample:

$$m_t = (10^{-3} \times V_t \times V_d (C_c)) / (A_t \times A_d) \qquad \text{Eq. 1}$$

Titration Procedure. Use the following equation to calculate the amount of CN^- in the sample:

$$m_t = (T - B) \times V_t \times 250 / (A_t \times Q_t) \qquad \text{Eq. 2}$$

8.5 Total Cyanide Concentration in Stack Gas.

Use the following equation to calculate total cyanide concentration in the stack gas:

$$C_s = K \times m_t / V_{m(std)} \qquad \text{Eq. 3}$$

Where:

$K = 1.00\ m^3/m^3$ if $V_{m(std)}$ is expressed in metric units.

$K = 35.31\ ft^3/m^3$ if $V_{m(std)}$ is expressed in English units

8.5 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively. To calculate V_s the average stack gas velocity, use equation 2-9 of Method 2 and the data from this field test.

9. ALTERNATIVE TEST METHODS FOR TOTAL CYANIDE.

9.1 NIOSH Method 7904 (Reference 10.4).
Airborne cyanides (gas and aerosol) are collected on a cellulose ester membrane filter and in a KOH bubbler. Because the particulate cyanide collected on the filter can liberate HCN which is trapped in the bubbler, the method cannot distinguish between HCN formed in this manner and HCN originally present in the air. Cyanide concentration is determined with an ion-specific electrode.
Interferences are significant. Sulfide, iodide, bromide, cadmium, zinc, silver, nickel, cuprous ion, and mercury are named as elements or compounds which affect the performance of the ion-specific electrode. Except for sulfide, the method does not propose remedies for minimizing or eliminating these interferences.

10. BIBLIOGRAPHY.

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

10.2 U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., Method 9010. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1982).

10.3 EPA-600/4-79-020. Method 335.2. In "Methods for Chemical Analysis of Water and Wastes" (Final report)/ J.F. Kopp et al. Environmental Monitoring and Support Laboratory, Cincinnati, OH. March 1983.

10.4 NIOSH Manual of Analytical Methods, 3rd ed., Method 7904, Cyanides, Aerosol and gas. U.S. Department of Health and Human Services DHHS (NIOSH) Publ. No. 84-100. Feb, 1984.

10.5 Same as Method 5, Citations 2 to 5 and 7 of Section 7.

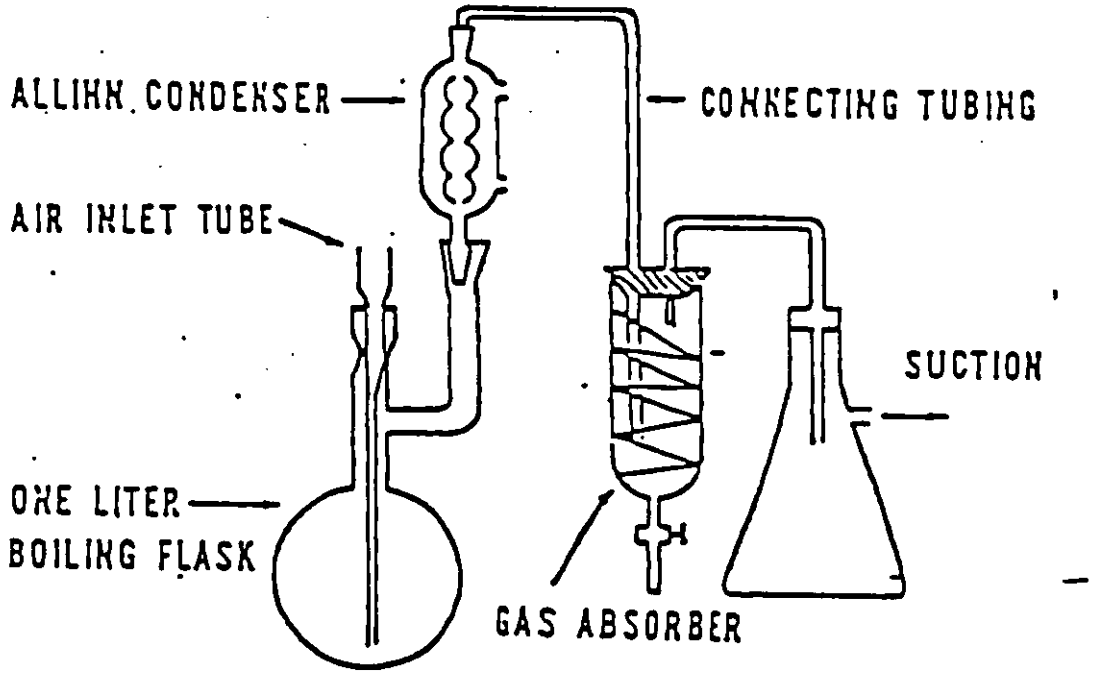


FIGURE 1

CYANIDE DISTILLATION APPARATUS

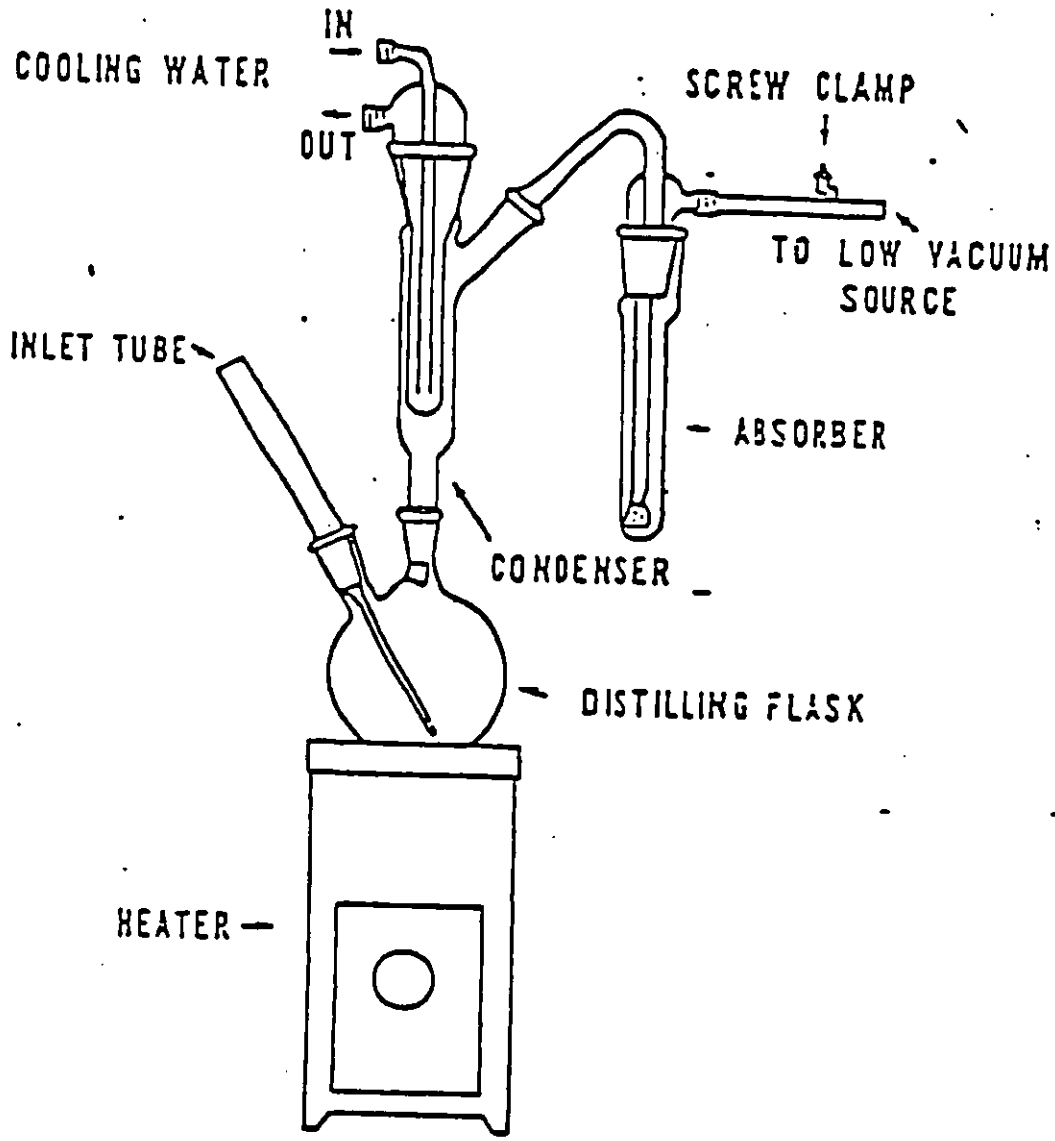


FIGURE 2
CYANIDE DISTILLATION APPARATUS

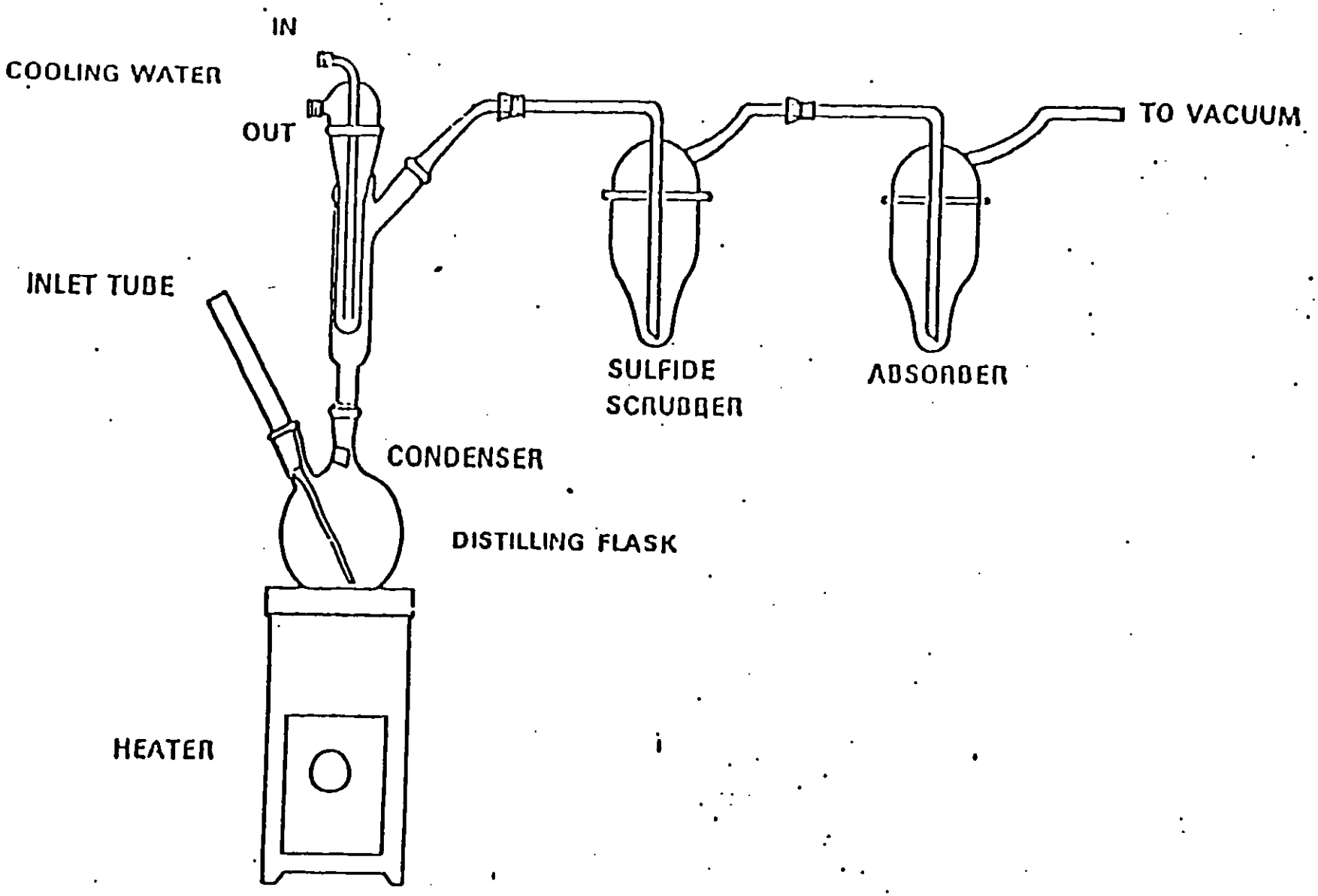


Figure 3.
Cyanide Distillation Apparatus

APPENDIX L

CARB Method 429

Determination of Polycyclic Aromatic Hydrocarbon Emissions from Stationary Sources

PAH's and Phenol

PAH emissions were determined exactly as detailed in CARB Method 429. Additional analysis, calibration and QA spiking was conducted for determination of phenol emissions by extending the GC/MS analysis scan.

State of California
Air Resources Board

Method 429

Determination of Polycyclic Aromatic Hydrocarbons Emissions From Stationary Sources

Adopted _____

TABLES

Table 1	POLYCYCLIC HYDROCARBONS
Table 2	ANALYTICAL PRACTICAL QUANTITATATION LIMITS
Table 3	COMPOUNDS TO BE USED FOR FIELD SPIKES
Table 4	IONS SPECIFIED FOR QUANTIFYING AND MONITORING PAH
Table 5	SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

FIGURES

Figure 1	PAH SAMPLING TRAIN
Figure 2	PARTICULATE SAMPLING TRAIN EQUIPPED WITH IN-STACK FILTER
Figure 3	CONDENSER AND SORBENT TRAP FOR COLLECTION OF GASEOUS PAH
Figure 4	PARTICULATE FIELD DATA SHEET
Figure 5	SAMPLE RECOVERY SCHEME
Figure 6	FLOWCHART FOR SAMPLE EXTRACTION AND CLEANUP FOR ANALYSIS

Method 429

Determination Of Polycyclic Aromatic Hydrocarbon(PAH) Emissions From Stationary Sources

1.0 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of polycyclic aromatic hydrocarbons (PAH) emissions from stationary sources. The sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample, as well as the original sample size and instrument sensitivity.

This method is restricted to use only by or under the supervision of analysts experienced in the use of capillary column gas chromatography/mass spectrometry and skilled in the interpretation of mass spectra.

Because of the toxicity of the materials known or believed to contain PAH, certain precautions must be taken which are necessary to prevent exposure to the analyst or to others.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to approval by the Executive Officer.

1.2 PRINCIPLE

Particulate and gaseous phase PAH are extracted isokinetically from the stack and collected on a filter, on XAD-2 resin, in the impingers, or in upstream sampling train components. Only the total amounts of each PAH in the stack emissions can be determined with this method. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH.

The analytical method entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts (if necessary) and analysis of the processed extract for PAH using high-resolution capillary column gas chromatography coupled with either low resolution mass spectrometry (HRGC/LRMS), or high resolution mass spectrometry (HRGC/HRMS).

Various performance criteria are specified herein which the analytical data must satisfy to ensure the quality of the data. These represent minimum criteria which must be incorporated into any program in which PAH emissions are determined from stationary sources.

The method presented here is intended to determine the total concentration of several PAH, commonly referred to as the EPA priority PAH compounds. They are listed in Table 1.

TABLE 1 POLYCYCLIC HYDROCARBONS

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benz[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Benzo[ghi]perylene
15. Dibenz[ah]anthracene
16. Indeno[1,2,3-cd]pyrene

1.3 MATRIX INTERFERENCES

Modified Method 5 sampling train can cause artifactual formation and PAH transformation. The fact that PAH can degrade or transform on sample filters is well documented. Certain reactive PAH such as benzo[a]pyrene, benzo[a]anthracene, and fluoranthene when trapped on filters can readily react with stack gases. Low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides have been known to react with these PAH.

PAH degradation may be of even greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water they are converted into sulfuric acid and nitric acid respectively. There is evidence that under such conditions certain PAH will be degraded. It is recommended that the levels in the impingers be used as a qualitative tool to determine if breakthrough has occurred in the resin.

In order to assess the effects of ozone, sulfur oxides and nitrogen oxides the tester is recommended to concurrently monitor for these gases during PAH sampling.

1.4 DEFINITIONS AND ABBREVIATIONS

1.4.1 Internal Standard

A component which is added to every sample and is present in the same concentration in every blank, quality control sample, and concentration calibration solution. It is added to the sample before injection and is used to measure the concentration of the analyte and surrogate compound.

1.4.2 Surrogate Standard

A component added to the sample matrix in a known amount and allowed to equilibrate with the matrix so that its measured concentration in the extract relative to an internal standard is an indication of the extraction efficiency. The surrogate standard is a component that can be completely resolved, is not present in the sample, and does not have any interference effects, (e.g. a perdeuterated PAH).

1.4.3 Relative Response Factor

The response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

1.4.4 Performance Standard

A mixture of known amounts of selected standard compounds; it is used to demonstrate continued acceptable performance of the GC/MS system. These include system performance checks, calibration checks, quality checks, matrix recovery, and surrogate recoveries.

1.4.5 Performance Evaluation Sample

A sample prepared by EPA or other laboratories containing representative PAH in known concentrations approximating those present in typical field samples.

1.4.6 Executive Officer

The phrase Executive Officer as used in this document shall mean the Executive Officer of the California Air Resources Board or Air Pollution Control Officer of the local air pollution control district/air quality management district at whose request the test is conducted, or his or her authorized representative.

1.5 PRACTICAL QUANTITATION LIMITS

Table 2 lists target practical quantitation limits for the PAH of interest.

PQL: The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

TABLE 2 ANALYTICAL PRACTICAL QUANTITATION LIMITS (ng/µL)

	LRMS	HRMS
1. Naphthalene	20	.05
2. Acenaphthylene	20	.05
3. Acenaphthene	20	.05
4. Fluorene	20	.05
5. Phenanthrene	20	.05
6. Anthracene	20	.05
7. Fluoranthene	20	.05
8. Pyrene	20	.05
9. Benz[a]anthracene	20	.05
10. Chrysene	20	.05
11. Benzo[b]fluoranthene	20	.05
12. Benzo[k]fluoranthene	20	.05
13. Benzo[a]pyrene	20	.05
14. Benzo[ghi]perylene	20	.05
15. Dibenz[ah]anthracene	20	.05
16. Indeno[1,2,3-cd]pyrene	20	.05

If 20 ug of sample is collected during a 3 hr. M5 run at 0.75 cu. ft./min. then with LRMS a PQL of 5 ug/m^3 can be obtained.

If 50 ng of sample is collected during a 3 hr. M5 run at 0.75 cu. ft./min. then with HRMS a PQL of 13 ng/m^3 can be obtained.

1.6 INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 5.8.6.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

A methyl silicone capillary column, will resolve the target PAH. Positive results using any other gas chromatographic column must be shown to be isomer specific.
If other gas chromatographic conditions or other techniques are used, the tester is required to substantiate the data through an adequate quality assurance program approved by the Executive Officer.

1.7 ESTIMATING PAH CONCENTRATIONS IN SAMPLE

Some estimate of PAH levels in the sample is necessary in order to specify which analytical method is used. This is because different levels of internal, surrogate, and spiking concentrations are added to samples depending on whether LRMS or HRMS is used for the analysis. For sources where ug/m^3 of PAH are found LRMS is sufficient. For sources where lower levels are found HRMS will be needed.

If possible, a pretest should be conducted and a pretest sample should be analyzed to estimate the PAH concentration found in the source. Where a pretest is not feasible the tester should estimate the concentration of PAH from the best available resources. After obtaining the estimated PAH concentration the tester will specify either HRMS or LRMS.

2.0 SAMPLE COLLECTION

2.1 SAMPLE RUNS, TIME, AND VOLUME

2.1.1 Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data, which is generallly three runs.

2.1.2 Sample Time

The sampling time must be of sufficient length to provide coverage of the average operating conditions of the source.

2.1.3 Sample Volume

The sample volume must be sufficient to provide the required amount of analyte to meet both the minimun detection limit MDL of the analytical method and the allowable stack emissions. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{b}$$

Where:

A = The analytical MDL in ng
B = Percent (%) of the sample used per analytical run
C = Estimated sample recovery (%)
D = Allowable stack emissions (ng/dscm)

2.2 SAMPLING TRAIN

The following apparatus and materials are appropriate for use in these procedures. Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

The following sampling apparatus is recommended. The tester may use an alternative sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

A schematic diagram of the sampling train is shown in Figure 1. The train consists of nozzle, probe, heated particulate filter, condenser, and sorbent module followed by two impingers and a silica gel drying cartridge. An in-stack filter may be used in place of the probe and heated filter if this is required. A cyclone or similar device in the heated filter box may be used for sources emitting a large amount of particulate matter.

For sources with a high moisture content, a water trap may be placed between the heated filter and the sorbent module. Additional impingers may also be placed after the sorbent module. If any of these options are used, details should be provided in the test report. The train may be constructed by adaptation of an EPA Method 5 train. Descriptions of the train components are contained in the following sections.

FIGURE 1 PAH SAMPLING TRAIN

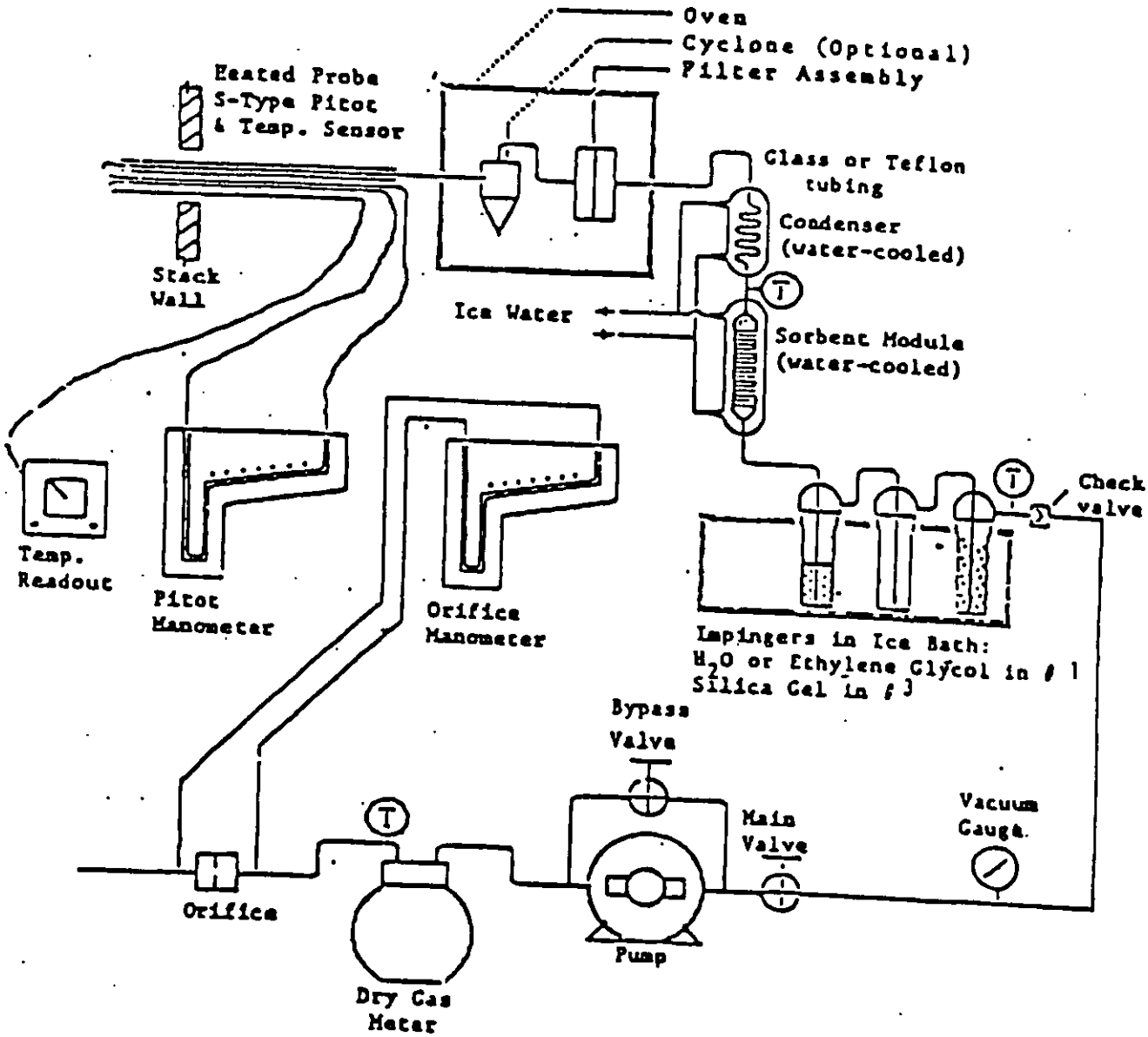
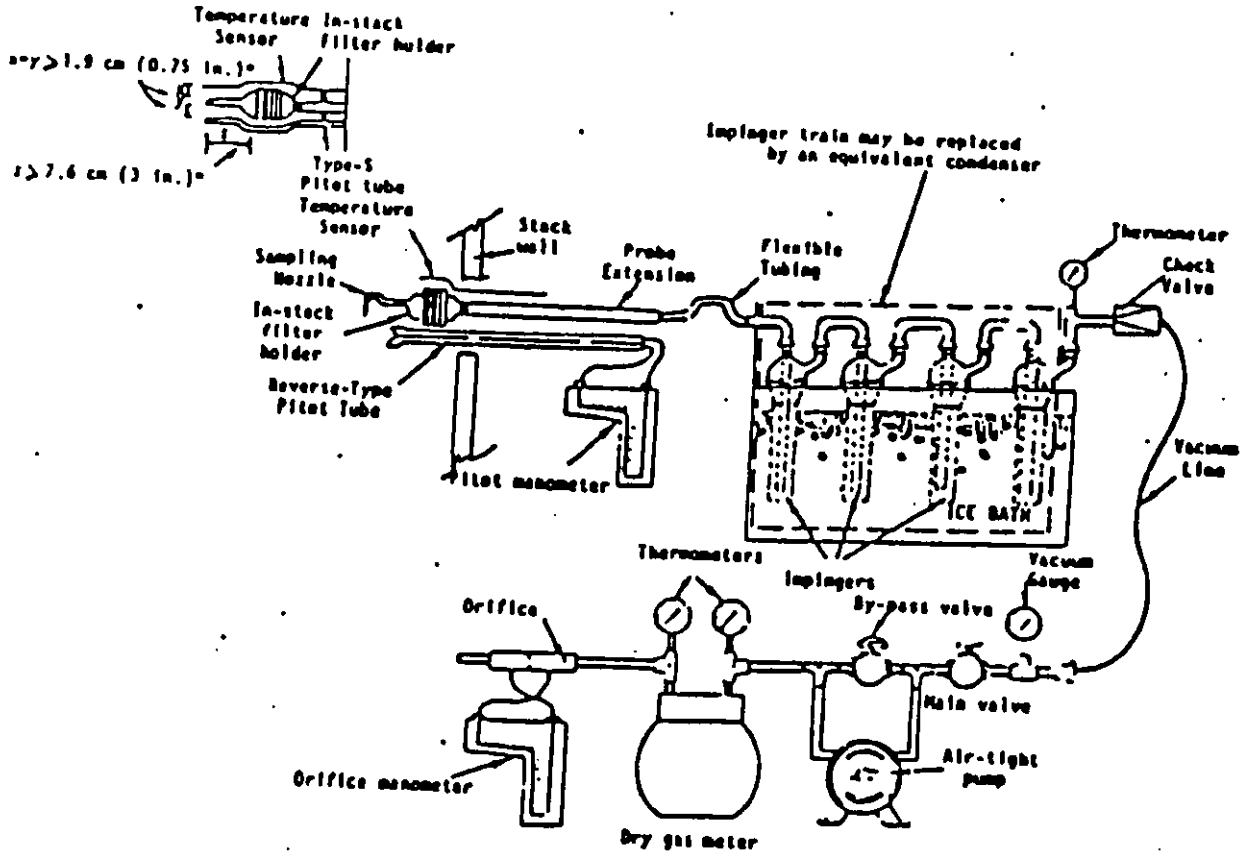


FIGURE 2 PARTICULATE SAMPLING TRAIN EQUIPPED WITH IN-STACK FILTER



* Suggested (interference-free) spacings

2.2.1 Probe Nozzle

Quartz, or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1 of ARB method 5.

2.2.2 Probe

The probe should be lined or made of Teflon, quartz, or borosilicate glass. The liner or probe is to provide an inert surface for the PAH in the stack gas. The liner or probe extends past the retaining nut into the stack. A temperature-controlled jacket provides protection of the liner or probe. The liner shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without the use of sealing greases. If an in-stack filter is used, the probe follows the in-stack filter.

2.2.3 Sample Transfer Line

The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings that are capable of forming leak-free, vacuum tight connections without using sealing greases. The line should be as short as possible.

2.2.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a glass frit filter support and glass-to-glass seal or Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe, cyclone, or nozzle depending on the configuration used. Other holder and gasket materials may be used subject to the approval of the Executive Officer.

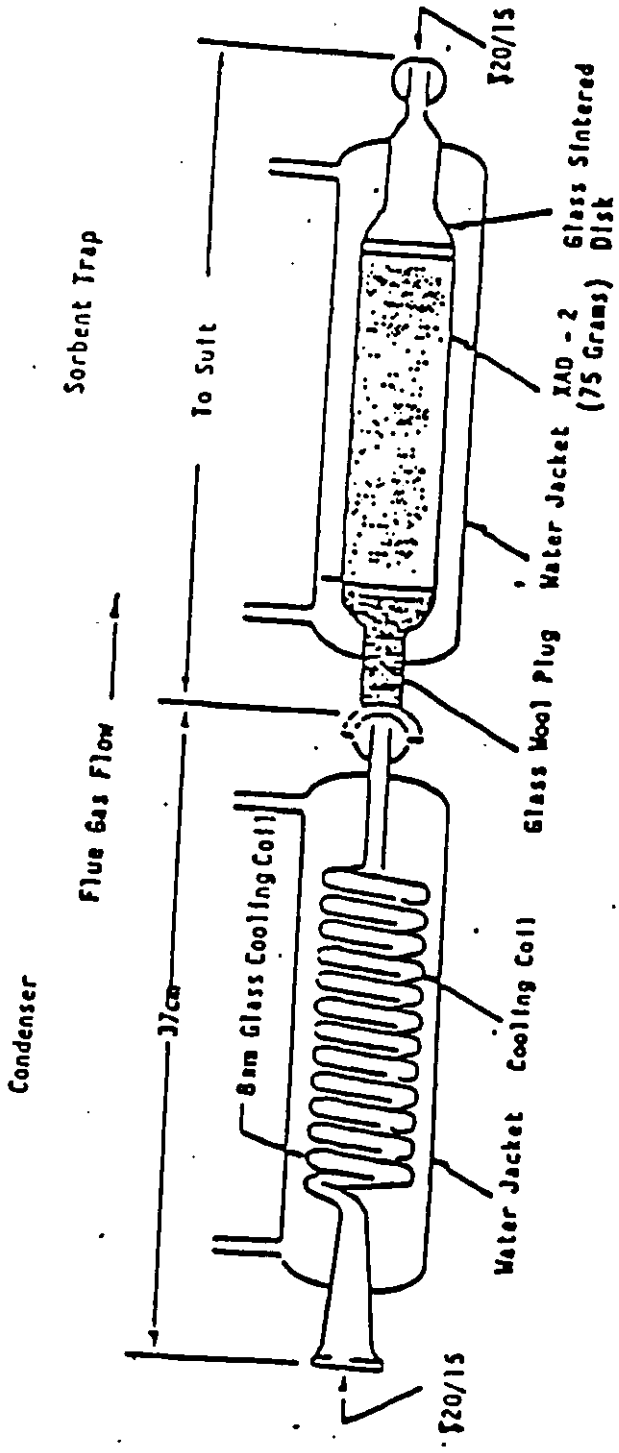
2.2.5 Preseparator

A cyclone, a high capacity impactor or other device may be used to remove the majority of the particles before the gas stream is filtered. This catch must be included in any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other materials may be used subject to the approval of the Executive Officer.

2.2.6 Condenser

The condenser shall be constructed of borosilicate glass and shall be designed to allow the cooling of the gas stream to at least 20°C before it enters the sorbent module. Design for the normal range of stack gas conditions is shown in Figure 3.

FIGURE 3. CONDENSER AND SORBENT TRAP FOR COLLECTION OF GASEOUS PAH



2.2.7 Sorbent Module

The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum tight seals without the use of sealant greases (Figure 3). The vertical resin trap is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must be cooled to 20 °C (68°F) or less. The gas temperature shall be monitored by a thermocouple placed either at the inlet or outlet of the sorbent module. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

2.2.8 Impinger Train

Two or more impingers are connected in series with connecting fittings able to form leak-free, vacuum tight seals without sealant greases. All 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 1.3 cm (1/2 in.)from the bottom of the flask.

The first impinger, connected to the outlet of the sorbent module shall be further modified to have a short stem, so that the sample gas does not bubble through the collected condensate. The first impinger shall be empty.

An oversized impinger may be required for sampling high moisture streams since this impinger collects the condensate which passes through the sorbent module for subsequent analysis. The second impinger initially contains water or alternatively 100 mL ethylene glycol which is intended to collect PAH not adsorbed by the resin.

A thermometer which measures temperatures to within 1°C (2°F), should be placed at the outlet of the second impinger.

2.2.9 Silica Gel Cartridge

This shall be sized to hold 200 to 300 gm of silica gel to absorb moisture, and to prevent damage to the pumping system.

2.2.10 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer shall be used to determine stack gas flow rate. The pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs with other sampling components as part of an assembly, the arrangements must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free arrangements are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

Source sampling assemblies that do not meet these minimum spacing requirements (or the equivalent of these requirements) may be used. However, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods which are subject to prior approval by the Executive Officer.

2.2.11 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (delta P) readings and the other for orifice differential pressure readings.

2.2.12 Metering System

Vacuum gauge, leak-free pump, thermometers accurate to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 1. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

2.2.13 Barometer

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

2.2.14 Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred configuration and alternative arrangements of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

2.2.15 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder during sampling of (120±14°C) (248±25°F). 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.

2.3 FILTERS

The in-stack filters shall be Teflon coated glass fiber filters, without organic binders or be Teflon membrane filters, and shall exhibit 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 2986-71.

Test data from the supplier's quality control program are sufficient for this purpose. Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control or contamination check to confirm that there are no contaminants present that will interfere with the analysis of selected species at the target detection limits.

Filter precleaning shall consist of soxhlet extraction, in batches not to exceed 50 filters, with the solvent(s) to be applied to the field samples. As a QC check, the extracting solvent(s) shall be subjected to the same concentration, clean-up and analysis precedures to be used for the field samples. The background or blank value observed shall be converted to a per filter basis and shall be corrected for any differences in concentration factor between the QC check (CF_{QC}) and the actual sample analysis procedure (CF_S).

$$\text{Blank value per filter} = \frac{\text{Apparent ug of analyte,}}{\text{No. filters extracted}} \times \frac{CF_S}{CF_{QC}} \leftarrow ?$$

Where:

$$CF = \frac{\text{Initial volume of extracting solvent}}{\text{Final Volume of concentrated extract}}$$

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depend not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-extracted and the solvent extracts re-analyzed until an acceptably low background level is achieved.

2.4 SORBENTS

2.4.1 Amberlite XAD-2 Resin

Resin may be purchased precleaned or the resin may be cleaned in accordance with the procedure presented in Section 7.1.2 of ARB Method 428. Precleaned resin must be checked for contamination as described in Section 2.4.2. If the resin fails the QC check, it may be re-cleaned. ?

2.4.2 QC Contamination Check

The XAD-2 resin, whether purchased precleaned or cleaned as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of resin, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of resin.

The XAD-2 resin aliquot shall be subjected to the same extraction, concentration, clean up, and analytical procedures as those applied to the field samples. The quantitative criteria for acceptable resin quality will depend on the detection limit criteria established for the field sampling and analysis program.

Resin which yields a background or blank signal greater than or equal to that corresponding to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that the acceptance limit for resin cleanliness depends not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

2.4.3 Silica Gel

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

2.4.4 Water

Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with Teflon-lined screw caps.

2.4.5 Crushed Ice

Place crushed ice in the water bath around the impingers.

2.4.6 Glass Wool, Silanized

Cleaned by thorough rinsing, i.e., sequential immersion in three aliquots of hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE-lined screw cap.

2.5 SAMPLING PROCEDURE

Because of the complexity of this method, testers should be trained and experienced with the test procedures in order to ensure reliable results.

2.5.1 Pretest Preparation

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

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to assembly of the train.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass or plastic petri dishes) and keep the filters in those containers at all times except during the sample weighing.

Record weight of filters to the nearest 0.1 mg.

2.5.2 Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to ARB Method 1 or as specified by the Executive Officer.

Determine the stack pressure, temperature, and the range of velocity heads using ARB Method 2; it is recommended that a leak-check of the pitot lines be performed (see ARB Method 2, Section 3.1).

Determine the moisture content using ARB Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings.

Determine the stack gas dry molecular weight, as described in ARB Method 2, Section 3.6. If integrated sampling (ARB Method 3) 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 ARB Method 4 sample run.

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

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

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Executive Officer), (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume determined in Section 2.1.2. The latter is based on an approximate average sampling rate.

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

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

2.5.3 Cleaning Glassware

All glass parts of the train upstream of and including the sorbent module and the first impingers should be cleaned as described in Section 3A of the 1974 issue of Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples (Reference 13.3). Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

All glassware should be rinsed with methylene chloride prior to use in the PAH sampling train.

2.5.4 Preparation of Amberlite XAD-2 Sorbent Trap

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned resin to fill completely the glass sorbent trap which has been thoroughly cleaned as prescribed and rinsed with hexane. Follow the resin with glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Figure 3 for details.

The dimensions and resin capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the PAHs.

2.5.5 Preparation of Collection Train

Keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Caution: Do not use sealant greases in assembling the sampling train.

If impingers are used to condense stack gas moisture, prepare them as follows: place 100mL of either water or ethylene glycol in the first impinger. Leave the second impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the silica gel cartridge.

Place the container in a clean place for later use in the sample recovery.

If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

Using tweezers or clean disposable surgical gloves, place a labeled (identified) filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed.

Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 1, or 2. Place crushed ice around the impinger.

2.5.6 Leak Check Procedures

2.5.6.1 Pretest Leak Check

A pretest leak-check is required. The following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize. Leak-check the train at the sampling site by plugging the nozzle with a Teflon plug and pulling a vacuum of at least 380 mm Hg (15 in. Hg).

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

Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in Section 4.1.4.1 of ARB Method 5 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse the direction of the by-pass valve. This will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as described below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

2.5.6.2 Leak Checks During Sample Run

If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. the leak-check shall be done according to the procedure outlined in Section 8.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume of gas sampled since the last leak check using the method of Section 2.8.2 of this protocol, or shall void the sampling run.

Immediately after component changes, leak-checks are to be done according to the procedure outlined in Section 2.5.6.1 above.

2.5.6.3 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 2.5.6.1 except that it shall be conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If,however, a higher leakage rate is obtained, the tester shall either, (1) record the leakage rate and correct the sample volume as shown in Section 2.8.2 of this method, or (2) void the sampling run.

2.5.6.4 Correcting for Excessive Leakage Rates

The equation given in Section 2.8.2 of this method for calculating v_m (std), the corrected volume of gas sampled, can be used as written unless the leakage rate observed during any leak-check after the start of a test exceeded L_a, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate exceeds L_a, then replace v_m in the equation in Equation 11-1 with the following expression.

$$v_m = (L_i - L_a)\Theta_i - (L_p - L_a)\Theta_p$$

where:

v_m	=	Volume of gas sampled as measured by the dry gas meter (dscf).
L_a	=	Maximum acceptable leakage rate equal to 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.
L_p	=	Leakage rate observed during the post-test leak-check, m^3/min (ft^3/min).
L_i	=	Leakage rate observed during the leak-check performed prior to the "ith" leakcheck (i = 1,2,3...n), m^3/min (ft^3/min).
Θ_i	=	Sampling time interval between two successive leak-checks beginning with the interval between the first and second leak-checks, min.
Θ_p	=	Sampling time interval between the last (n th) leak-check and the end of the test, min.

Note: Substitute only for those leakage rates (L_i or L_p) which exceed L_a.

2.5.7 Train Operation

During the sampling run maintain a sampling rate within 10 percent of true isokinetic, unless otherwise specified or approved by the Executive Officer. For each run, record the data required on the sample data sheet shown in Figure 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

Take other readings required by Figure 4 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate.

Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream.

Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85±0.02, and the stack gas equivalent density (dry molecular weight) (M_d) is equal to 29±4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Citation 7.5) are taken to compensate for the deviations.

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

FIGURE 4 PARTICULATE FIELD DATA

Run No. _____
Location _____
Date _____
Operator _____
Meter Box No. _____
Local Time.
Start/Stop _____

Pitot Tube Factor _____
Probe Tip Dia, in. _____
Probe Length _____
Sample Train
Leak Test
Before _____ After _____
Pitot Tube
Leak Test
Before _____ After _____

Project No. _____
Plant Name _____
Ambient Temp °F _____
Meter Temp °F _____
Bar. Press, "Hg _____
Stack Press, "H_2O _____
Assumed Moisture, % _____
Heater Box Setting, °F _____
Probe Heater Setting, °F _____

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Point	Clock Time	Dry Gas Meter, CF	Pitot in. H_2O & P	Orifice ΔH in H_2O		Impinger Temp. °F	Filter Box Temp. °F	Stack Temp. °F	Pump Vacuum in. Hg
				Desired	Actual				
Start									

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

Traverse the stack cross-section, as required by ARB Method 1 or as specified by the Executive Officer, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes; this minimizes the chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain the temperature at the condenser outlet below 20°C (68°F). This will prevent excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced during a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check as outlined in Section 2.5.6.2. The total particulate weight shall include the combined catches of all filter assemblies.

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

Note that when two or more trains are used, a separate analysis of the collected particulate from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the particulate catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 2.5.6.3. Also, leak-check the pitot lines as described in Section 3.1 of ARB Method 2; the lines must pass this leak-check, in order to validate the velocity head data.

2.5.8 Calculation of Percent Isokinetic Variation

Calculate percent isokinetic variation (see Section 2.8.4) to determine whether another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Executive Officer for possible variance on the isokinetic rates.

2.6 CALIBRATION

The tester shall maintain a laboratory log of all calibration data which shall be obtained using the standard equipment and procedures indicated below.

2.6.1 Probe Nozzle

Probe nozzles shall be calibrated according to the procedure described in Section 5.1 of ARB Method 5.

2.6.2 Pitot Tube

The procedure for calibrating the Type S pitot tube assembly is outlined in section 4 of ARB Method 2.

2.6.3 Metering System

Calibration of the metering system shall be performed according to the requirement of Section 5.3 of ARB Method 5.

2.6.4 Temperature Gauges

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

2.6.5 Leak Check of Metering System Shown in Figure 1

The tester shall use the procedure outlined in Section 5.6 of ARB Method 5.

2.6.6 Barometer

Calibrate against a mercury barometer.

2.7 QUALITY ASSURANCE/QUALITY CONTROL

The positive identification and quantification of PAH in this assessment of stationary combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section are to be used to monitor the performance of the sampling methods, identify problems, and effect solutions.

2.7.1 Field Blanks

Field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and should be handled with exactly the same procedure as the samples.

2.7.2 Blank Train

At least 10 percent of the trains in each series of test runs, and a minimum of one of these trains shall be a blank train. Prepare and set up the blank train in a manner identical to that described above for the sampling trains. The blank train shall be taken through all of the steps from preparation to leak-check without actual sampling. Recover the blank train as described in Section 3.4.

2.7.3 Spiked PAH Sampling Trains

Spiked trains are required as a means of estimating the precision and accuracy of the sampling train for collecting and recovering PAH in the stack gas sample. Isotopically labelled PAH shall be spiked onto the filter and/or the XAD-2 resin prior to each test.

At least 30% of the trains in each series of test runs shall be spiked. In the case where the control efficiency of an air pollution control device is evaluated, there shall be a minimum of one spiked train at the inlet and one at the outlet of the control devices. Table 6 shows a spiking plan for method internal standards, recovery internal standards, and field spikes. Additional labelled PAH may also be used if available. The labelled PAH used in the field spike must be different from the quantitative internal standards. The appropriate spike level will depend on the source to be tested. If the spiking scheme must be modified, the analyst must demonstrate that the proposed plan will generate data of satisfactory quality. Acceptable field spike recoveries should range between 50 and 150 percent.

TABLE 3 COMPOUNDS TO BE USED FOR FIELD SPIKES

FIELD SPIKE FOR FILTER	FIELD SPIKE FOR RESIN
benzo[a]anthracene-d_{12}	methyl-naphthalene-d_{10}

Note: Add prior to sampling.

2.8 SAMPLING CALCULATIONS

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

NOMENCLATURE FOR SAMPLING CALCULATIONS

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

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

C_s - Concentration of PAH in stack gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

G_s - Total mass of PAH in stack gas sample, ng.

I - Percent isokinetic sampling.

L_a - Maximum acceptable leakage rate for either a pretest leak-check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i - Individual leakage rate observed during the leak-check conducted prior to the "ith" component change (i = 1, 2, 3, ...n), m^3/min (cfm).

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

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

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

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

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

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

T_m = Absolute average dry gas meter temperature (see Figure 3), ^oK (^oR). Note: T_m will depend on type of meter used and sampling configuration.

T_s = Absolute average stack gas temperature ^oK (^oR).

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

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

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

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

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

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

Y = Dry gas meter calibration factor.

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

t_t = Total sampling time, min.

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

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

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

13.6 = Specific gravity of mercury.

60 = sec./min.

100 = Conversion to percent.

2.8.1 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet, Section 2.5.7 (Figure 4).

2.8.2 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg) by using Equation 2-1.

Equation 2-1

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

Where:

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

$$= 17.65\ ^{\circ}R/in.\ Hg \text{ for English units}$$

NOTE: Equation 2-1 can be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L.

If L_p or any L_i exceeds L_a, Equation 2-1 must be modified as follows:

(a) Case I.
No component changes made during the sampling run. In this case, replace V_m in Equation 2-1 with the expression:

$$V_m' = V_m - (L_p - L_a)\, t_t$$

(b) Case II.

One or more component changes made during the sampling run. In this case, replace V_m in Equation 2-1 with the expression:

$$V_m'' = V_m - \sum_{i=2}^{n} (L_i - L_a)\, t_i - (L_p - L_a)\, t_p$$

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

2.8.3 Conversion Factors

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

2.8.4 Isokinetic Variation

2.8.4.1 Calculation From Raw Data

Equation 2-2

$$I = \frac{100\, T_s\, [K_3 V_{1c} + (V_m/T_m)\,(P_{bar} + \Delta H/13.6)]}{60\, t\, v_s\, P_s\, A_n}$$

Where:

K_3 = 0.003454 [(mm Hg m^3)/(ml ^oK)] for metric units

= 0.002669 [(in Hg ft^3)/[(ml ^oR)] for English units

2.8.4.2 Calculation from Intermediate Values

Equation 2.3

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

$$= K_4 \frac{T_s\, V_{m(std)}}{P_s\, v_s\, t\, A_n\, (1 - B_{ws})}$$

Where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

2.8.5 Acceptable Results

If 90 percent < I < 110 percent, the results are acceptable. If there is a high bias to the results, i.e., I < 90 percent, then the results are defined as at or below the determined value and the Executive Officer may opt to accept the results. If there is a low bias to the results, i.e., I > 110 percent, then the results are defined as at or above the determined value, and the Executive Officer may opt to accept the results. Otherwise, reject the results and repeat the test.

3.0 SAMPLE RECOVERY

3.1 CLEANING PROCEDURE

Glassware cleaning. Glassware used in the sample recovery procedure must be cleaned by detergent and water, and rinsed with tap water, deionized water, acetone, toluene, and methylene chloride. Other cleaning procedure may be used as long as acceptable method blanks are obtained.

Aluminum foil cleaning. Aluminum foil should be cleaned with acetone followed by hexane. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

3.2 APPARATUS

Probe Nozzle Brush: Inert bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

Wash Bottles: Teflon wash bottles are recommended.

Glass Sample Storage Containers: Narrow mouth amber glass bottles 500 mL or 1000mL. Screw cap liners shall be Teflon.

Filter Storage Containers: Sealed filter holder or precleaned, wide-mouth amber glass containers with Teflon lined screw caps.

Graduated Cylinder and/or Balance: To measure condensed water to within 2 mL or 1 g. Use a graduated cylinder that has a minimum capacity of 500 mL, and subdivisions no greater than 2 mL.

Storage Containers: Air tight metal containers to store silica gel.

Rubber Policeman: To aid in transfer of silica gel to container. A rubber policeman is not necessary if silica gel is weighed in the field.

Funnel: Glass or Teflon may be used.

Ground Glass Caps or Aluminum Foil: To cap off adsorbent tube and the other sample-exposed portions of the train.

Aluminum Foil: Heavy-duty, precleaned to meet QA standards.

3.3 SAMPLE RECOVERY REAGENTS

Water: Deionized (DI), then glass distilled, and stored in glass containers with Teflon-lined screw caps.

Acetone: Nanograde quality, "Distilled in Glass" or equivalent, stored in original containers.

Hexane: Nanograde quality, "Distilled in Glass" or equivalent, stored in original containers.

Toluene: Nanograde quality, "Distilled in Glass" or equivalent, stored in original containers.

Methylene Chloride: Nanograde quality or equivalent.

3.4 SAMPLE RECOVERY PROCEDURE

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with a ground glass cup or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean, and enclosed so that the chances of contaminating or losing the sample will be minimized.
No smoking is allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, broken filters, color of the impinger liquid, etc. Treat the samples as follows:

Sample Container No. 1 (filter):
Carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. If it is necessary to fold the filter, make sure that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

Sorbent Modules:
Remove the sorbent module from the train and cap it off.

Cyclone Catch:
If the optional cyclone is used, quantitatively recover the particulate matter into a sample container and cap.

Sample Container No. 2 (Front half rinses):
Quantitatively recover material deposited in the nozzle, probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with methanol, toluene, and methylene chloride three times each. Place all these rinses in Container No.2.

Sample Container No. 3 (Back half rinses):
Rinse the back half of the filter holder, the connecting line between the filter and the condenser (if using the separate condenser-sorbent trap) three times each with methanol, toluene and methylene chloride, and collect all rinses in Container No. 3. If using the combined condenser/sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2 portion. If the optional water knockout trap has been employed, the contents and rinses shall be placed in Container No. 3. Rinse it three times each with methanol, toluene, and methylene chloride.

Sample Container No. 4 (First impinger):
Remove the first impinger. wipe off the outside of the impinger to remove excess water and other material. Pour the contents and rinses directly into Container No. 4. Rinse the impinger sequentially three times with methanol, toluene, and methylene chloride.

Sample Container No. 5 (Second Impinger):
Remove the second impinger, wipe the outside to remove excess water and other debris. Empty the contents and rinses into Container No. 5. Rinse each with distilled water three times.

Sample Preservation and Handling:
Maintain samples (except filters) at 0-4°C from the time of collection to extraction and protect from light. Filters should be stored on dry ice. Begin sample extraction within seven days of collection and analyze within 40 days of extraction.

4.0 ANALTICAL PREPARATION

4.1 INTERFERENCES

If samples contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. As an alternative two cleanup procedures which are listed in Section 4.7 may be used. The final option is to use an HPLC clean up procedure. A detailed HPLC procedure is beyond the scope of this method. If such a method is used the analyst must meet the same performance criteria as for the other methods.

4.2 ANALYSIS: SAMPLE PREPARATION

All sample preparation should be done under yellow lights to limit sample degradation.

4.3 SAFETY

The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the information of the analyst (7.7-7.9).

The following parameters covered by this method have been tentatively classified as known or suspect, human or mammalian carcinogens; benzo(a)anthracene, dibenzo(a,h) anthracene. A guideline for the safe handling of carcinogens can be found in section 5209 of Title 8 of the California Administrative Code.

4.4 APPARATUS

Glassware Cleaning:
Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) must be cleaned as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, toluene, and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Clean aluminum foil with appropriate solvents e.g. acetone followed by hexane.

Grab Sample Bottle:
Amber glass, 125-mL and 250-mL, fitted with screw caps lined with Teflon.

Concentrator Tube, Kuderna-Danish:
10 mL, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

Evaporative Flask, Kuderna-Danish: 500-mL

Snyder Column, Kuderna-Danish: Three-ball macro.

Snyder Column, Kuderna-Danish: Two-ball micro.

Minivials:
1.0 mL vials; cone-shaped, heavy wall borosilicate glass; with Teflon-faced rubber septa and screw caps.

Soxhlet Apparatus:
1 liter receiver, 1 heating mantle, condenser, soxhlet extractor.

Rotary Evaporator

Nitrogen Blowdown Apparatus

Analytical Balance:
Capable of accurately weighing to the nearest 0.0001 g.

4.5 ANALYSIS PREPARATION: REAGENT

Reagent water: Deionized (DI), glass distilled

Hexane: Nanograde quality or equivalent.

Toluene: Nanograde quality or equivalent.

Tetradecane: Nanograde quality or equivalent.

Methyl Alcohol: Nanograde quality or equivalent.

Methylene Chloride: Nanograde quality or equivalent.

Sulfuric Acid: ACS. Reagent Grade Concentrated, sp. gr. 1.84.

Sodium Sulfate:
ACS. Reagent Grade Granular, anhydrous. Purify by heating in an oven at 400 °C for four hours or by extracting with methylene chloride and drying in a hood for 4 or more hours in a shallow tray. Store in a bottle with Teflon lined screw cap and store bottle in a desiccator.

Silica Gel:
For column chromatography, type 60, EM reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate in a foil covered glass container for longer than 16 hours at 130 °C, then store at 130°C.

Alumina:
Acidic Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190 °C.

Alumina:
Basic, Woelm activity grade I or equivalent (activate at 600 °C for 24 hours).

NOTE: The performance of alumina in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall check the activity of each new batch of alumina to ensure that PAH recovery is satisfactory. The lowest level calibration standards shall be used for this check. Recovery of each native PAH standard shall be at least 70%.

4.6 ANALYSIS

Stack sampling will yield both liquid and solid samples for PAH analysis. Samples may be analysed separately as recovered according to Section 3.4 or they may be combined as follows:

1) Particulate filter and particulate matter collected on the filter (Section 3.4), cyclone catch (Section 3.4) and Sample Container No. 2 (Section 3.4).

2) Sample Container No. 3 (Section 3.4), Resin (Section 3.4) and rinse of resin cartridge.

3) Sample Containers No. 4, and No. 5 (Section 3.4).

This sample recovery scheme is shown in Figure 5. It is preferable that samples not be split prior to analysis even when they might appear homogeneous as in the case of single liquid phase samples. Solid samples such as the resin are not homogeneous, and filter samples are generally so small that the desired minimum detection limit might not be attained if the sample were split.

A flowchart of the extraction and cleanup procedures is presented in Figure 6.

4.6.1 Extraction of liquid Samples:

A. Front end rinses, Sample Container No. 2:

Concentrate the rinse from sample container No. 2 (Section 3.4) to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen) while heating the sample gently on a water bath at 50°C. Concentrate to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates and proceed as described under Section 3.4.

B. Resin Rinses, Sample Container No. 3:

Concentrate the rinses from sample container No. 3 (Section 3.4) to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen) while heating the sample gently on a water bath at 50°C. Concentrate to near dryness. Combine this residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the resin sample, and proceed as described under Section 3.4.

C. Impinger and Impinger Rinses, Containers No. 4 and No.5:

Place the combined contents of Sample Containers No. 4, and No. 5 (Sections 3.4) in a separatory funnel. Add an appropriate quantity of the surrogate standard mixture to achieve the concentration recommended in Section 5.2.5, and extract the sample three times with aliquots of methylene chloride. Combine the organic fractions and pour through Na_2SO_4 into a round bottom flask. Add approximately 500 uL tetradecane. Concentrate to 500 uL with a Kuderna-Danish concentrator or rotoevaporator, then transfer the extract to an 8-mL test tube with hexane. Proceed with sample cleanup procedures below (Section 4.6.2).

FIGURE 5. SAMPLE RECOVERY SCHEME

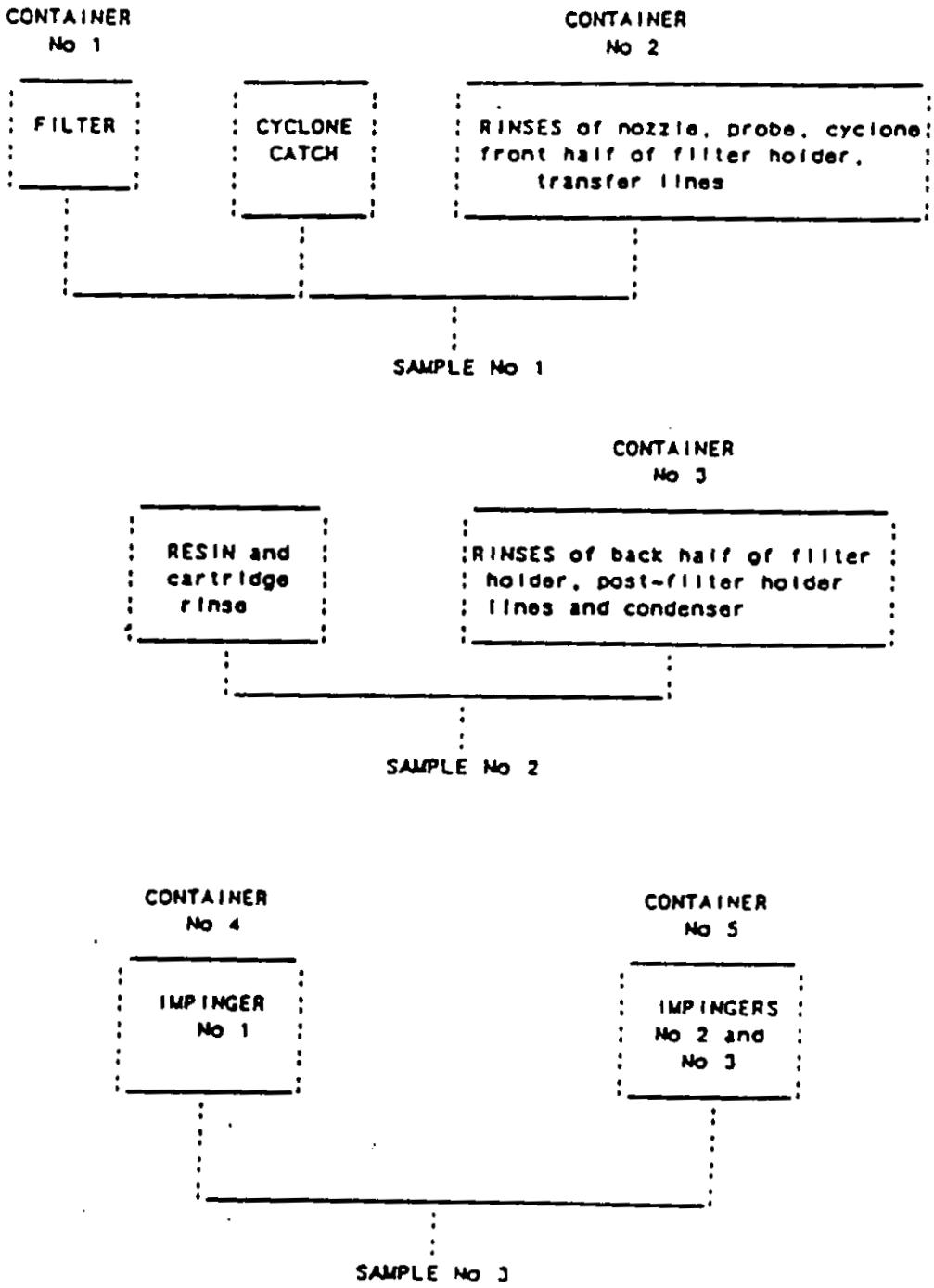
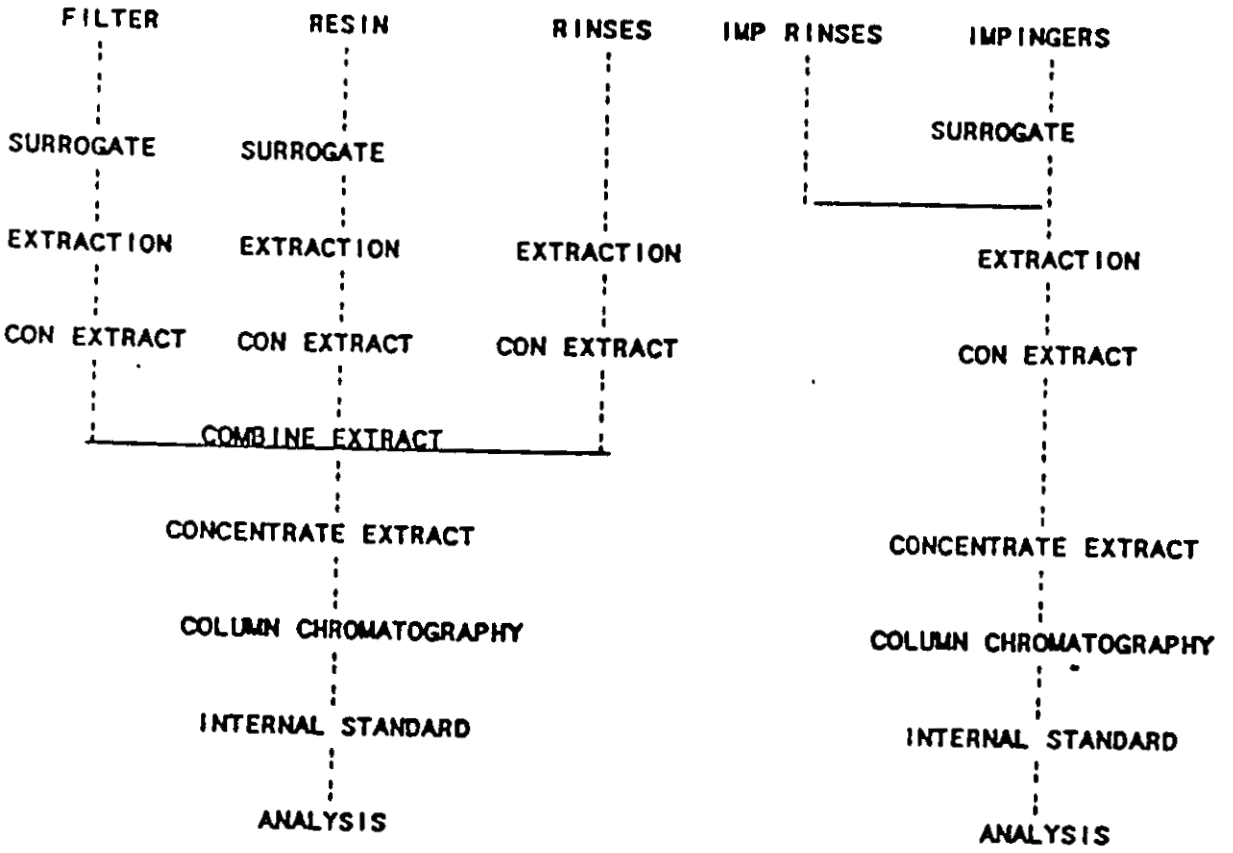


FIGURE 6. FLOWCHART FOR SAMPLE EXTRACTION AND CLEANUP FOR ANALYSIS OF PAH IN STACK GAS SAMPLE



4.6.2 Extraction of Solid Samples

A. Filter and Particulate Matter:

The Soxhlet apparatus should be cleaned by an 8-hr. Soxhlet, and the solvent discarded. Add 20 g Na_2SO_4 to the thimble. Cut the filter into small strips and place the entire sample and residue rinses (4.6.1) on top of the Na_2SO_4. Mix immediately and add the appropriate quantity of the surrogate standard solution to obtain the extract volume concentrations suggested in Section 5.2.5.

Place the thimble in the Soxhlet apparatus, and add 250 mL of benzene or toluene to the receiver. Assemble the Soxhlet, turn on the heating controls and cooling water, and reflux for 16 hours. After extraction, allow the Soxhlet to cool. Transfer to a 500 mL round bottom flask, and add approximately 500 uL of tetradecane. Add approximately 50 mL of hexane and concentrate the extract volume to 500 uL with a Kuderna-Danish concentrator or rotary evaporator. Transfer the extract to an 8 mL test tube with hexane and set aside for column cleanup if needed (Section 4.7).

B. Resin:

Clean the Soxhlet apparatus as written in Section 3.1. The resin sample volume will most likely be too large for extraction in a single Soxhlet. In such cases, the sample can be divided into two portions. Surrogate standard solution should also be divided into two approximately equal portions. Combine one of these resin portions with the residue rinses and proceed with each extract as in Section 4.6.3.

4.6.3 Combining Extracts

Combine concentrated extracts from the three sample containers 1, 2, 3, with the cyclone, filter and resin. Combine extracts from the impingers and impinger rinses and keep separate from the other combined extract and analyze separately.

4.7 PRECLEAN-UP

The analyst may directly analyze the extracted samples. If there are interferences in the direct analysis then a preclean up step is required.

Several column chromatographic cleanup options are available. Either of the two described below, the silica and alumina column procedures, are considered to be sufficient. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to generate acceptable accuracy and precision as required in Section 5.

An extract obtained as described in the foregoing sections is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively (with rinsings) to either of the columns described below.

4.7.1 Column Preparation

A. Silica Gel Column: Pack a glass gravity column (250 mm x 10 mm) in the following manner:

Insert a glass wool plug (cleaned) into the bottom of the column and add a slurry of 10 grams of activated silica gel (4.5) in methylene chloride and a 1 cm layer of anhydrous sodium sulfate (Section 4.5).

B. Acid Alumina Column: Pack a 10 mm glass gravity column as follows:

Insert a glass wool plug (cleaned) into the bottom of the column. Add 6 g of acid alumina prepared as described in Section 4.5. Tap the column gently to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

4.7.2 Column Chromatography Procedure

A. Silica Gel Column: Preelute the column with 40 ml of pentane. The rate for all elutions should be about 2 ml/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 ml sample extract onto the column using an additional 2 ml of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 ml of pentane and continue the elution of the column.

Next, elute the column with 25 ml of methylene chloride/pentane (2:3)(v/v). Concentrate the collected fraction using K-D apparatus or a rotary evaporator to required sample volume.

B. Alumina Column:

Elute the column with 50 ml of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow.

Transfer 1 ml of the sample extract onto the column. Rinse out extract vial with 1 ml hexane and add it to the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column.

Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 ml of hexane. If the extract is in 1 ml of hexane, and if 1 ml of hexane was used as a rinse, then 13 ml of additional hexane should be used. Collect the effluent and concentrate to desired volume.

Transfer to a minivial using a hexane rinse and concentrate to the desired volume using a gentle stream of nitrogen. Store the extracts in a freezer away from light until GC/MS analysis.

5.0 ANALYTICAL DETERMINATION

5.1 APPARATUS

5.1.1 Gas Chromatograph

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical column and gases. On column injection is preferred but splitless injection is acceptable.

5.1.2 Column

A high resolution cross-linked methyl silicone fused silica capillary column.

5.1.3 Mass Spectrometer

Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volt (nominal) electron energy in the electron impact ionization mode. Alternatively, a high resolution mass spectrometer may be used.

5.1.4 GC/MS Interface

Any gas chromatograph to mass spectrometer interface may be used as long as it gives acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (Section 5.3).

5.1.5 Data System

A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits.

5.2 REAGENTS

5.2.1 Stock standard solutions (1.00 µg/uL)

Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.2.2 Preparation of Stock Solutions

When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

Store stock standard solutions in Teflon-sealed screw-cap bottles at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

Stock standard solutions must be replaced after 1 year, or sooner, if comparison with quality control check samples indicates a problem.

5.2.3 Internal Standard Solutions

The internal standard recommended is 2,2'-difluorobiphenyl-d_4. Other compounds may be used as internal standards as long as the requirements given in Section 5.3.5 are met. Each 1-mL sample extract undergoing analysis should be spiked with 10ul of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard for LRMS. For HRMS the resulting IS concentration should be 0.3ng/uL. Store at 4 °C or less when not being used.

5.2.4 Calibration Standards

Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit: The others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. For LRMS the range should be 20ng/uL to 200ng/uL. For HRMS the range should be 0.1ng/uL to 5 ng/uL. Each standard should contain each analyte for detection by this method. Each calibration standard is spiked with a solution of surrogate standards. The resulting surrogate concentration should be midway on the calibration curve. Each 1-mL aliquot of calibration standard should be spiked with 10ul of internal standard solution prior to analysis.

All standards should be stored at -10°C to -20°C and should be freshly prepared if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.2.5 Surrogate Standards

Listed in table 5 are the labeled isotopes used for surrogates. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

TABLE 4

IONS SPECIFIED FOR QUANTIFYING AND MONITORING PAH

Compounds	Primary* Quantitation Ion	Secondary Confirmation Ion(s)	Methane Chemical Ionization Ion(s)
Naphthalene	128	129,127	129,157,169
Acenapthalene	152	151,153	152,153,181
Acenaphthene	154	153,152	154,155,183
Fluorene	166	165,167	166,167,195
Phenanthrene	178	179,176	178,179,207
Anthracene	178	176,179	178,179,207
Fluoranthene	202	101,203	203,231,243
Pyrene	202	200,203	203,231,243
Benzo[a]anthracene	228	229,226	228,229,257
Chrysene	228	226,229	228,229,257
Benzo[b]fluoranthene	252	253,125	252,253,281
Benzo[k]fluoranthene	252	253,125	252,253,281
Benzo[a]pyrene	252	253,125	252,253,281
Benzo[ghi]perylene	276	138,277	276,277,305
Dibenz[ah]anthracene	278	139,279	278,279,307
Indeno[1,2,3-cd]pyrene	276	138,227	276,277,305

*Just use primary ion for HRMS quantification and identification

TABLE 5

SEMIVOLATILE SURROGATE STANDARDS

naphthalene-d_8

acenapthalene-d_8

acenaphthene-d_{10}

fluorene-d_{10}

phenanthrene-d_{10}

anthracene-d_{10}

fluoranthene-d_{10}

pyrene-d_{10}

benzo[a]anthracene-d_{12}

chryene-d_{12}

benzo[b]fluoranthene-d_{12}

benzo[d]fluoranthene-d_{12}

benzo[a]pyrene-d_{12}

benzo[ghi]perylene-d_{12}

5.2.6 Matrix Spike Standard

Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.3 INITIAL CALIBRATION

5.3.1 GC Operating Conditions

The recommended GC/MS operating conditions:

initial column temperature and hold time, 40 °C for 4 min
column temperature program: 40-270°C at 10°C/min
final column temperature hold 270°C (until benzo[g,h,i]perylene has eluted)

injector temperature: 250-300°C
specifications
injector: Grob-type, splitless
sample volume: 1-2 ul
carrier gas: Hydrogen at 50 cm/sec or helium at 30cm/sec

5.3.2 MS Operating Condition

mass range: 35-500amu
scan time: 1sec/scan
source temperature: According to manufacturer's specifications transfer line temperature: 250-300°C

5.3.3 GC/MS Tuning Criteria

Background subtraction should be straight forward and designed only to eliminate column bleed or instrument background ions.

The analyst should tune the MS to achieve optimum performance at unit resolution for LRMS and either 3000, 5000, or 10,000 for HRMS.

Mass spectral peak profiles for m/z 69 (LRMS only), 219 and 264 must be recorded, plotted, and reported. The scan should include a minimum of +/- two peaks (i.e, m/z 67-71 for the m/z 69 profile for LRMS or +/- 100 ppm for HRMS at 10,000).

5.3.4 GC Performance Criteria

A mixture of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), benzidine and pentachorophenol should be used to test for column performance. Degradation of DDT to 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (DDE) and 2,2-bis(4-chlorophenyl)-1,1-dichlorethane (DDD) should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in of the capillary column.

Column resolution. The column resolution criteria of 75% valley between benzo[b]fluoranthene and benzo[k]fluoranthene is required.

5.3.5 Isotope Dilution and Internal Standard Criteria

Calibration with isotope dilution is used when (1) labelled compounds are available, (2) interferences do not preclude its use, and (3) the quantitation mass extracted ion current profile (EICP) are for the compound is in the calibration range. If any of these conditions preclude isotope dilution, internal standard method is used.

5.3.6 System Performance Check Compounds (SPCC)

A system performance check must be performed to ensure that minimum average RFs are met before the calibration is used. The System Performance Check Compounds are: N-nitroso-di-n-propylamine, hexachlorocyclopentadiene; 2,4-dinitrophenol, and 4-nitrophenol. The minimum acceptable average RF for these compounds SPCCs is 0.050. These compounds must meet the minimum requirement when the system is calibrated.

5.4 DAILY CALIBRATION

5.4.1 Daily Tuning Criteria

Prior to analysis of samples, the GC/MS tuning standard must be analyzed. This is the same criteria as in the initial tuning criteria given in section 5.3.3. These criteria must be demonstrated during each 12-hr. shift.

5.4.2 Calibration Standard Check

A calibration standard(s) at mid-level concentration containing all the semivolatile analytes, including all required surrogates must be performed every 12-hr. during analysis. Compare the response factor data from the initial calibration for a specific instrument as per the SPCC (Section 5.4.3) and CCC (Section 5.4.4) criteria.

5.4.3 System Performance Check Compounds (SPCCs)

A system performance check must be made during every 12 hr. shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. This check must be met before analysis begins.

5.4.4 Calibration Check Compounds (CCCs)

After the system performance check is met, CCCs, acenaphthene, napthalene, fluoranthene, benzo[a]pyrene, and chrysene are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{RF_I - RF_c \times 100}{RF_I}$$

Where:

RF_I = average response factor from initial calibration

RFc = response factor from current verification check standard.

If the difference for any compound is greater than 20 percent, the laboratory should consider this a warning limit. If the difference is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12hr), the chromatographic system must be inspected for malfunctions and corrections must be made as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

5.5 GC/MS ANALYSIS

It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

Spike the 1-mL extract obtained from sample preparation with 10uL of the internal standard solution just prior to analysis. Analyze the 1-mL extract by GC/MS using a 30-m x 0.25-mm (or 0.32-mm) silicone-coated fused-silica capillary column. For LRMS the volume to be injected should ideally contain 100 ng of surrogates for a 1 uL injection. For HRMS the volume to be injected should ideally contain 2 ng of surrogate per injection. The recommended GC/MS operating conditions to be used are specified in Section 5.3.2.

If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be re-analyzed.

Perform all qualitative and quantitative measurements as described in Sections 5.6 and 5.7. Store the extracts at 4°/C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

5.6 QUALITATIVE ANALYSIS

5.6.1 MS Criteria

For LRMS an analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours of the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. For HRMS selective ion monitoring the use of exact mass measurement is used as a confirmation of identity.

5.6.2 Relative Retention Time RRT Criteria

The sample component RRT must compare within 0.06RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

5.6.3 Ion Criteria

All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

5.6.4 Relative Intensities

The relative intensities of ions specified in Section 5.6.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

5.7 QUANTITATIVE ANALYSIS

When a compound has been identified, the quantitation of that compound will be by the isotope dilution technique. If isotope dilution is not possible then the method of internal standards is used.

5.7.1 Isotope Dilution

A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (pollutant to labeled) vs concentration in standard solutions is plotted using linear regression. Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

The relative response of a pollutant to its labeled analog is determined from isotope ratio values computed from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured for the pure pollutant.

R_y = the isotope ratio measured for the labeled compound.

R_m = the isotope ratio of an analytical mixture of pollutant and labelled compounds.

The m/z's are selected such that $R_x > R_y$. If R_m is not between $2R_x$, and $0.5R_y$, the method does not apply and the sample is analyzed by internal standard method.

When there is GC and spectral separation of the pollutant-labelled pair:

$R_x = [A_p]$ A_p = Area of pollutant

$R_y = 1\backslash[A_i]$ A_i = Area of isotope

$RR = R_x \times R_y$

RR = Relative response

If significant GC and spectral overlap occur, RR is computed using the following equation:

$$RR = (R_y - R_m)\ (R_x + 1)/(R_m - R_x)\ (R_y - 1)$$

If the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, and averaged relative response/concentration ratio may be used for that compound, otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

5.7.2 Internal Standard Method

The internal standard method is used only when isotope dilution cannot be used.

Calibration requires the determination of response factors (RF) which are defined by the following equation:

$$RF = (A_s \times C_{is})/(A_{is} \times C_s)$$

A_s is the area of the characteristic mass for the compound in the standard.

A_{is} is the area of the characteristic mass for the internal standard.

C_{is} is the concentration of the internal standard

C_s is the concentration of the compound in the standard

The response factor is determined for at at least five concentrations appropriate to the reposnse of each compound. The amound of internal standard added to each extract is the same so that C_{is} remains constant. The RF is plotted vs concentration for each compound in the standard to produce a calibration curve.

If the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an average response factor may be used for that compound; otherwise the complete calibration for that compound shall be used over the 5 point range.

5.7.3 Report Results

When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

5.8 QUALITY CONTROL/QUALITY ASSURANCE

Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

5.8.1 Quality Check Sample

Quality Check Sample: A quality (QC) check sample which contains all the analytes is required. The sample matrix of the filter and or resin is spiked to contain 100ug/sample for LRMS or 0.5ng/sample for HRMS.

The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

Analyze the well-mixed QC check samples according to the method beginning in Section 4.6 with extraction of the samples.

5.8.2 Quality Check Standard Acceptance Criteria

Calculate the average recovery in ug/sample. Acceptable recoveries are 50% to 150%.

When one or more of the analytes tested fail at the recovery acceptance criteria, the analyst must proceed according to this Section.

Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 5.8.1.

Beginning with Section 5.8.1 repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 5.8.1

5.8.3 Surrogate Standard Acceptance Criteria

Recoveries: To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

If recovery is not within the limits of 50%-150% then, the following procedures are required.

Re-extract and reanalyze the sample if no calculation or instrument problems are found.

If there is a non-discernable problem, flag the data as "estimated concentration".

5.8.4 Matrix Spike Acceptance Criteria

Matrix Spike:

The concentration of the spike in the sample should be determined as follows:

The spike should be at 1 to 5 times higher than the background concentration.

Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 5.8.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike. The recovery must be within 50%-150%.

If a specific analyte percent recovery falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 5.8.1.

QC Check Standard for compounds that fail acceptance criteria. If any analyte fails the acceptance criteria for recovery in Section 5.8.2, a QC check standard containing each analyte that failed must be prepared and analyzed.

Note: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. The QC check standard should be routinely analyzed with the spiked sample.

5.8.5 QC Check Standard Recovery

Analyze the QC check standard to determine the concentration measure (A) of each analyte. Calculate each percent recovery (ps) as 100(A/T)%, where T is the true value of the standard concentration.

Compare the percent recovery (ps) for each analyte with the QC acceptance criteria of 50%-150%. Only analytes that failed the test in Section 5.8.2 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

5.8.6 Reagent Blank

Before processing any samples, the analyst should demonstrate through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

5.8.7 Field Blanks and Spikes

During sampling the test crew is required to take field blanks, a blank train and a spiked sample train.

Field Blanks and Field Blank Train:
The field blank will be used to analyze for background levels. The blank analytical preparation and analysis will run concurrently with the other test samples.

Field Spike Trains:
The field spike trains are required to determining the recoveries of both the analytical and sampling method. These samples are to be run concurrently with the other test samples. Acceptable recoveries are between 50% to 150%. If the values are outside this range then the data must be flagged as " estimated concentration".

Duplicate Samples: These are individual samples that are analyzed more than once to obtain the precision of the analytical method. At least one duplicate should be analyzed per test.

5.8.8 Additional Quality Assurance

The laboratory shall adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies. In recognition of the advances ocurring in chromatography, the analyst is permitted certain options to improve separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedures described in Section 5.8 and demonstrate the ability to generate data of acceptable accuracy and precision.

5.9 ALTERNATIVE TEST METHOD

If an alternative test method is used, the tester must demonstrate the alternative test method is equivalent to the method specified herein to the satisfaction of the Executive Officer. The Executive Officer will require the submission of data showing that the quality assurance (QA) program of the alternate method is equivalent to the QA program specified heretofore.

6.0 REPORTING

6.1 MINIMUM DETECTABLE CONCENTRATION

The minimum detection limit for the the individual PAH are determined from the following equations:

EQUATION 6-4

$$\text{Concentration, ng/dscm} = \frac{Q_i \times A_s}{V_{m(std)} \times A_{is} \times RR}$$

Where:

RR = Relative response factor calculated according to Equation 6-5.

Q_{is} = Amount of internal standard added to each sample.

A_s = Mean noise for the PAH mass chromatogram at the m/z shown in Table 4.

A_{is} = MS response for the internal standard ion

NOTE Any dilution factor introduced by following the procedure in Section 5 should be applied to this calculation.

6.2 RELATIVE RESPONSE FACTORS

This is determined from the following equation using the data obtained in Section 5 from the analysis of the calibration standards.

EQUATION 6-5

$$RR = \frac{A_s \times C_{ss}}{A_{ss} \times C_s}$$

A_s = MS response for the native ion at m/z given in Table 4.

C_{ss} = Concentration of the appropriate surrogate standard, ng/uL.

A_{ss} = MS response of the appropriate surrogate standard.

C_s = Concentration of the native ion of interest.

6.3 PERCENT RECOVERY OF SURROGATE STANDARD

Calculate the percent recovery, R_{is} for each internal standard in the sample extract, using Equation 6-6.

EQUATION 6-6

$$R_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times RF_r \times Q_{ss}} \times 100\%$$

Where:

A_{is} = Area of quantitation ion of the internal standard.

Q_{is} = ng of internal standard.

6.4 THE RESPONSE FACTOR FOR DETERMINATION OF RECOVERY

Calculate using data obtained from the analysis of the calibration standards according to Equation 6-7.

EQUATION 6-7

$$RF_r = \frac{A_{ss} \times C_{is}}{A_{is} \times C_{ss}}$$

Where:

C_{rs} = Concentration of the internal standard.

6.5 RESULTS

Any deviations from the procedures described in this protocol shall be documented in the analytical and sampling report.

6.6 CONCENTRATION OF PAH IN STACK GAS

Determine the concentration of PAH in the stack gas according to Equation 6-8.

EQUATION 6-8

$$C_s = K_5 \frac{G_s}{V_{m(std)}}$$

6.7 CONCENTRATION OF INDIVIDUAL PAH COMPOUNDS

The concentration of individual PAH compounds are determined from the following equations:

EQUATION 6-9

$$\text{Concentration, ng/dscm} = \frac{Q_{ss} \times A_s}{V_{m(std)} \times A_{ss} \times RR}$$

Where:

RR = Relative response factor calculated according to Equation 6-5.

Q_{ss} = Amount of surrogate standard added to each sample.

A_s = MS response for native ion at the m/z shown in Table 4.

A_{ss} = MS response for the surrogate standard ion

NOTE: Any dilution factor introduced by following the procedure in Section 5 should be applied to this calculation.

7 REFERENCES

7.1 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 8270. Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

7.2 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3611. Alumina Column Cleanup and Separation of Petroleum Wastes. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

7.3 U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3630. Silica Gel Cleanup. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

7.4 Thomaspon, J.R., ed., Analysis of Pesticide Residues in Human and Environmental Samples, Environmental Protection Agency, Research Triangle Park, N.C. (1974).

7.5 ARB Method 428. Determination of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Emissions From Stationary Sources. November, 1987.

7.6 U. S. Environmental Protection Agency, Method 1625 Revision B - Semivolatile Organic Compounds by Isotope Dilution. 40 CFR Ch.1 (7-1-85 Edition) Pt. 136, App. A.

7.7 "Carcingogens-Working with Carcinogens, " Department of Health Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977

7.8 "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

7.9 "Safety in Academic Chemistry Laboratories, "American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

APPENDIX M

CARB Method 430

Determination of Formaldehyde in Emissions from Stationary Sources

FORMALDEHYDE and ACETALDEHYDE

Formaldehyde emissions were determined following the protocol detailed in CARB Method 430.

Acetaldehyde emissions were determined by analysis of the acetaldehyde peak of the HPLC chromatogram developed following Method 430.

Additional calibration was performed to quantify the acetaldehyde emissions.

State of California
Air Resources Board

Proposed Method 430

Determination of Formaldehyde in Emissions From Stationary Sources

Adopted _____

Method 430 Determination of Formaldehyde in Emissions From Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method applies to the determination of formaldehyde in emissions from stationary sources. The method is based on the use of high performance liquid chromatography (HPLC).

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to approval by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer or Air Pollution Control Officer of the state or local air pollution control agency at whose request the test is conducted, or his or her authorized representative.

1.2 Principle

Gaseous emissions are drawn through two midget impingers in series, each containing an aqueous acidic solution of 2,4-dinitrophenylhydrazine (DNPH). Formaldehyde reacts with DNPH by nucleophilic addition on the carbonyl followed by 1,2-elimination of water and the formation of the 2,4-dinitrophenylhydrazone. Acid is required to promote protonation of the carbonyl because DNPH is a weak nucleophile.

After organic solvent extraction, the DNPH-formaldehyde derivative is determined using reverse phase HPLC with an ultraviolet (UV) adsorption detector operated at 360 nm.

Formaldehyde in the sample is identified and quantified by comparison of retention times and area counts, respectively, with those of standard samples.

2. RANGE AND SENSITIVITY

Formaldehyde contamination of reagents can impair sensitivity levels. With careful attention to reagent purity and other relevant factors, a target detection limit of 400 ng/sample can be achieved with this method.

3. SAMPLING RUNS, TIME, AND VOLUME

3.1 Sampling Runs

The number of sampling runs must be sufficient to provide minimal statistical data and should not be less than three (3).

3.2 Sample Time

Sampling time and appropriate sampling rate should be chosen to obtain the sample volume estimated in Section 3.3 without exceeding the absorbing capacity of the impinger solution. If a single sampling run cannot reflect the variability of the process, the tester can consider a representative range of operating conditions by collecting several samples in sequence.

3.3 Sample Volume

The sample volume must be sufficient to provide the required amount of analyte to meet both the minimum detection limit (MDL) of the analytical method and the regulatory limit. If there is no regulatory limit, the target should be the typical concentration in emissions from the type of source being tested. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

Where:

A = The analytical MDL in ng
B = Percent (%) of the sample required per analytical run
C = Sample recovery (%)
D = Regulatory limit, or other target concentration as described above (ng/dscm)

4. INTERFERENCES

The DNPH formaldehyde derivative is easily separated by HPLC from the derivatives of other carbonyl compounds with which DNPH reacts.

Formaldehyde contamination of DNPH reagent can be a problem even after recrystallization. The DNPH must be purified and used within 48 hours of preparation.

5. APPARATUS

The following sampling apparatus is recommended. The tester may use an alternative sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method. It is recommended that all equipment which comes in contact with the sampled gas stream be of stainless steel, glass or Teflon unless these materials are found unsatisfactory and other materials demonstrated to be suitable in specific situations.

5.1 Sampling Train

A schematic diagram of the sampling train is shown in Figure 1.

5.1.1 Probe: Glass or other material as appropriate for the stack temperature, equipped with a glass wool plug to remove particulate matter if necessary. A probe is recommended only if the stack temperature does not allow direct insertion of the sample line (5.1.2).

5.1.2 Sample Line: Heated Teflon tubing, 6.4 mm (1/4 inch) outside diameter. Should be as short as possible, but long enough to allow insertion in the stack away from the diluted stream resulting from inleakage of ambient air.
To reduce the risk of sample contamination, new unused tubing shall be used for each series of samples considered to constitute an emissions test.

5.1.3 Fittings: Leak tight Teflon-to-glass connections to connect teflon tubing to the impingers, and to the rotameter.

5.1.4 Needle Valve: To adjust sample flow rate.

5.1.5 On-Off Valve: Teflon. To isolate impinger system for leak check.

5.1.6 Pump: Leak free, with capacity of at least 2 liters per minute.

5.1.7 Sampling System: Capable of accurately and precisely sampling 500-1000 mL/minute of gas sample (Figure 2). Ideally a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at intermediate points during the sampling period, and at the end of the sampling period to determine sample volume. The dry test meter may not be accurate at flows below 500 mL/minute, and should then be replaced by recorded flow readings at the start, finish, and every fifteen minutes during the collection.

5.1.8 Flow meter: Rotameter type or equivalent, with measurement range of 0.1 to 1.0 liters per minute for observing sampling rate. Ideally, a rotameter should be used at the system outlet to allow observation of the flow rate without interruption of the sampling process. To calibrate the rotameter, use a soap bubble flow meter or calibrated wet test meter connected to the flow exit. This assumes that the entire system is sealed.

5.1.9 Impingers: Wheaton micro impingers (25 mL) with grease free threaded connection between impinger and sample container, or equivalent. The bottom part of each impinger is a vial which can be removed after use and capped with a Teflon-lined screw cap before storage.

5.1.10 Ice bath: For cooling the impingers during sampling.

5.1.11 Friction top Metal Can: (e.g., 1-gallon paint can) - to hold sample vials

5.2 Sample Recovery

The following items are needed:

5.2.1 Wash Bottles (2): Teflon.

5.2.2 Sample Storage Containers: Chemically resistant, borosilicate glass bottles, for impinger and probe solutions and washes, 1000 mL.

5.3 Analysis

The following equipment is needed:

5.3.1 High Performance Liquid Chromatograph: A gradient HPLC system complete with column supplies, mobile phase reservoir, high pressure pumps; high pressure syringes, and all required accessories, including an injection valve or an automatic sampler with an optional 25-uL loop injector; compatible strip chart recorder; A data system is recommended for measuring peak areas and retention times.

5.3.1.1 Column: C-18 reverse phase (RP) column (30 cm x 3.9 mm ID)

5.3.1.2 Detector: Variable wavelength UV detector operating at 360 nm.

5.3.1.3 Pump: Gradient pumping system - constant flow.

5.3.2 Gelman AcroPrep syringeless 0.45 mm PTFE membrane sample filter units.

5.3.3 Filtration and degassing system such as Waters Part e85124 for filtering and degassing mobile phase solvents.

5.3.4 Pipettes: Various sizes, 1 to 10 mL.

5.3.5 Volumetric Flasks: Various sizes.

5.3.6 Graduated Cylinder: 1 L, for preparing the HPLC mobile phase

5.3.7 Syringe: 100 - 250 uL appropriate for HPLC injection.

5.3.8 Erlenmeyer Flask: 1 L, for preparing the HPLC mobile phase

5.3.9 Special glass apparatus for rinsing, storing, and dispensing saturated DNPH stock reagent (Figure 3)

5.3.10 Bottles: 10 oz., glass, with Teflon-lined screw cap for storing DNPH reagent.

5.3.11 Kuderna-Danish (K-D) Apparatus:

(a) Concentrator Tube: 10 mL, graduated (Kontes-K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of the extracts.

(b) Evaporation Flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

(c) Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

5.3.12 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

5.3.13 Water Bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

5.3.14 Analytical Balance: 0.1 mg sensitivity.

5.3.15 Polyethylene Gloves: used to handle the treated impingers.

6. REAGENTS

Unless otherwise specified, American Chemical Society (ACS) reagent grade (or equivalent) chemicals shall be used.

(Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used).

6.1 Sampling

6.1.1 Water: Deionized, distilled, charcoal filtered.

6.1.2 Impinger Solution: 0.05% DNPH/2N HCl reagent prepared as described in Section 7.4.

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

6.1.4 Quartz Wool: Cleaned by extracting with a 70/30 (v/v) hexane/methylene chloride mixture. Dry in a 110°C oven, and store in a solvent (6.3.7) washed glass jar with Teflon-lined screw cap.

6.1.5 Ice: For water bath for cooling the impingers during sampling.

6.1.6 Nitrogen: compressed gas cylinder - 99.999% purity.

6.2 Sample Recovery

6.2.1 Recovery Solvent: Methanol. Reagent grade. A blank must be screened by the analytical method.

6.3 Analysis

6.3.1 Reagent Water: Same as 6.1.1.

6.3.2 DNPH: 2,4-Dinitrophenylhydrazine (DNPH) - Aldrich Chemical (Catalog #D19,930-3) reagent grade or equivalent. Recrystallize (Section 7.1) at least twice with UV grade acetonitrile before using in standards.

6.3.3 Acetonitrile: UV grade, Burdick and Jackson "distilled-in glass," or equivalent.

6.3.4 Mobile Phase: 60% acetonitrile/40% water (v/v). Prepared as described in Section 9.2.

6.3.5 Hexane: Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent. A blank must be screened by the analytical method.

6.3.6 Methylene chloride: Pesticide quality or equivalent.

6.3.7 Extraction Solvent: Hexane/methylene chloride, 70/30 (v/v).

6.3.8 Sodium sulfate: ACS reagent grade. Granular, anhydrous. Purify by extracting with the extraction solvent (6.3.7), then air drying and heating in an oven at 400°C for at least four hours. Store in a solvent rinsed glass bottle with Teflon lined screw cap.

6.3.9 Hydrochloric acid: Reagent grade.

6.3.10 Formaldehyde: Reagent grade.

6.3.11 Charcoal: Activated, granular.

6.3.12 Helium: High purity grade.

7. PREPARATION OF REAGENTS

7.1 Purification of 2,4-Dinitrophenylhydrazine (DNPH)

NOTE: This procedure should be performed under a properly ventilated hood.

7.1.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

7.1.2 After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

7.1.3 Let covered beaker heat at this temperature range, allowing 95% of solvent to evaporate slowly.

7.1.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile.

(CAUTION: The following effects are attributed to the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systematic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death depending upon concentration and length of exposure period).

7.1.5 Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95 percent of the solvent has evaporated.

7.1.6 Repeat rinsing process as described in Section 7.1.4.

7.1.7 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 2N hydrochloric acid per 100 mL of DNPH solution, and analyze by HPLC. An ideal impurity level is shown in Figure 2.

7.1.8 The impurity level of DNPH should be below the sensitivity (ppb, v/v) expected for the anticipated sample volume. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

7.1.9 A special glass apparatus (Figure 3) should be used for the final rinse and storage according to the following procedure:

7.1.9.1 Transfer the crystals to the special glass apparatus (Figure 3).

7.1.9.2 Add 20 mL of acetonitrile, agitate gently, and let solution equilibrate for 10 minutes.

7.1.9.3 Drain the solution by properly positioning the three-way stopcock. (NOTE: The purified crystals should not be allowed to contact laboratory air except for a brief moment. This is accomplished by using the DNPH-coated silica on the gas inlet of the special glass apparatus.)

7.1.9.4 After draining, turn stopcock so drain tube is connected to measuring reservoir.

7.1.9.5 Introduce acetonitrile through measuring reservoir.

7.1.9.6 Rinsing should be repeated with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis. The impurity level should be comparable to that shown in Figure 2.

7.1.10 If the special glass apparatus is not available, transfer the purified crystals to an all-glass reagent bottle, add 200 mL of acetonitrile, stopper, shake gently, and let stand overnight. Analyze supernatant by HPLC according to Section 8.4. The impurity level should be comparable to that shown in Figure 2.

7.1.11 After purification, purity of the DNPH reagent can be maintained by storing in the special glass apparatus.

7.2 Preparation of DNPH-Formaldehyde Derivative

7.2.1 Titrate a saturated solution of the recrystallized DNPH in 2N HCl with formaldehyde.

7.2.2 Filter the colored precipitate, wash with 2N HCl and water and let the precipitate air dry.

7.2.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination table or HPLC analysis.

7.3 Preparation of DNPH-Formaldehyde Standards

7.3.1 Standard Stock Solution: Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in mobile phase (6.3.4).

A stock solution of approximately 100 mg/L is prepared by dissolving 10 mg of the solid derivative in 100 mL of mobile phase.

7.3.2 Calibration Standards: Prepare at least 5 concentration levels. Add accurately measured volumes of the stock solution to volumetric flasks and dilute to volume with mobile phase. One concentration should be near but above the method detection limit, while the other concentrations should correspond to the expected range of concentrations in real samples, or should define the working range of the detector.

7.3.3 Storage of Standards: Store all standard solutions in a refrigerator. They should be stable for approximately two months.

7.4 Preparation of Impinger Solution

NOTE: This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plastic ware must be scrupulously cleaned first by washing with soap and water, then rinsing several times with hot water followed by distilled deionized water (6.1.1). Aldehyde free acetonitrile should be used for the final rinse. Contact of reagents with laboratory air must be minimized.

Each batch of impinger solution must be prepared and purified within 48 hours of sampling, according to the following procedure:

7.4.1 Place 250 mg of solid 2,4-dinitrophenylhydrazine and 90 mL of concentrated HCl in a 500 mL volumetric flask and fill the flask to the mark with reagent water. Invert the flask several several times or sonicate until all of the solid material has dissolved.

7.4.2 Place approximately 400 mL of the DNPH reagent (7.4.1) in a 16 ounce glass bottle with a Teflon-lined screw cap. Add approximately 50 mL of a 70/30 (v/v) hexane/methylene chloride mixture to the bottle and shake the capped bottle on a reciprocating shaker for 15 minutes. Decant as much as possible of the organic layer, and then use a disposable pipette to remove the remainder. Discard the organic layer.

7.4.3 Extract the DNPH reagent two more times as described in 7.4.2. Cap the bottle tightly, seal with teflon tape, and place in a friction top can (5.1.11) containing a 1 to 2 inch layer of granular charcoal (6.3.11). Keep the bottle in the sealed can prior to use.

7.4.4 Prior to use, analyze a portion of the DNPH reagent according to the procedure described in Section 8.4. The

impurity level of DNPH should be below the sensitivity (ppb, v/v) level expected for the proposed sample volume. If the impurity level is not acceptable for the intended sampling application, repeat the extraction.

8. PROCEDURE

8.1 Sampling:

Because of the complexity of this method, testers should be trained and experienced with the test procedures in order to ensure reliable results.

8.1.1 Pretest Preparation: Dispense 15 mL of the DNPH/HCl solution (7.4) into each impinger vial. Cap the vials tightly, seal with Teflon tape, and place in a friction-top metal can for shipment to the sampling location. Section 7.4 specifies a maximum storage time of 48 hours from preparation of the solution to sampling

8.1.2 Preliminary Determinations: Prior to sample collection, install the entire assembly (including a "dummy" sampling impinger) and check the flow rate at a value near the desired rate. In general, flow rates of 500-1000 mL/minute should be employed. Flow rates greater than 1000 mL/min should not be used because collection efficiency of the impinger solution may decrease.

Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the start, finish, and every 15 minutes during the collection.

Ideally, a rotameter should be included, even when a dry gas meter is used, to allow observation of the flow rate without interruption of the sampling process.

The flow meter or dry gas meter must be calibrated (9.1) before and after each test.

8.1.3 Preparation of Collection Train: Before sampling, remove the glass vials from the friction-top metal can. Let the vials warm to ambient temperature before connecting them to the sample train. To reduce contamination, keep all openings of the sampling train covered until just prior to assembly, or until sampling is about to begin. Assemble the sampling train as shown in Figure 1. Using polyethylene gloves, connect the impingers in series to the sampling train so that the short end of the first impinger is attached to the probe.

8.1.4 Leak-Check Procedures: Before sample collection, install the entire assembly (including "dummy" sampling impingers)

and check for leaks. Turn off the "on/off" Teflon valve at the input end of the sampling system. The flow meter should not indicate any air flow through the sampling apparatus. Relieve the sample line vacuum before stopping the sample pump to prevent back flow of the impinger solution.

8.1.5 Sampling Train Operation: Record the following parameters on the sampling data sheet (Figure 4): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, sampling impinger ID, and dry gas meter pump identification numbers.

Turn on the sampler, and adjust the flow to the desired rate. A typical range is 0.5 to 1.0 L/min.

Operate the sampler for the desired period, with periodic recording of the variables listed in Figure 4.

At the end of the sampling period, record the parameters listed above and stop the sample flow. If a dry gas meter or equivalent total flow indicator is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and the end of the sampling period differ by more than 15%, the sample should be marked as suspect.

8.2 Sample Recovery

Inspect the sampling train prior to and during disassembly and note any abnormal conditions. Disconnect the impingers using polyethylene gloves, and treat them as follows:

8.2.1 Sampling Impingers: Cap the second impinger vial, seal with Teflon tape, and place in a friction-top can containing 1-2 inches of granular charcoal. Rinse the sample line and probe, if one is used, with reagent water, and add the rinse solution to the first impinger vial. Store both vials in the friction-top can and refrigerate until extraction and HPLC analysis.

All samples must be extracted within 7 days of collection and completely analyzed within 30 days of extraction.

8.2.2 Recovery Solution Blank: Save a total volume of water equal to that used for rinsing the probe.

8.3 Sample Preparation and Storage

8.3.1 Extraction: All samples must be extracted within 7 days of collection.

8.3.1.1 Shake the sample vials in a horizontal position on a reciprocating shaker for 10 minutes.

8.3.1.2 Remove the vials from the shaker, and extract with 10 mL of 70/30 (v/v) hexane/methylene chloride in the same manner as described in 8.3.1. Remove the organic layer with a disposable pipette, and retain in an Erlenmeyer flask.

The extraction may alternatively be carried out in a separatory funnel.

Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation.

8.3.1.3 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask. Other concentration devices or techniques such as nitrogen blowdown may be used in place of the K-D concentrator if the requirements of Section 10.3 are met.

8.3.1.4 Pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of hexane/methylene chloride extraction solvent and add it to the column to complete the quantitative transfer.

8.3.1.5 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml of extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (80°-90°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

8.3.2 Solvent Exchange: Before HPLC analysis, the extraction solvent must be exchanged to acetonitrile.

8.3.2.1 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 5 mL of acetonitrile, a new boiling chip, and reattach the macro Snyder column. Concentrate the extract as described in Section 8.3.1.5.

8.3.2.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of acetonitrile. A 5-mL syringe is recommended for this operation. Adjust the final extract volume to 5.0 mL.

8.3.3 Sample Storage: Transfer the extract to a Teflon-sealed screw-cap vial and store refrigerated at 4°C until analysis. All samples must be completely analyzed within 30 days of extraction.

8.4 Analysis

The method is restricted to use by or under the supervision of analysts experienced in the use of high performance liquid chromatography and the interpretation of the resulting chromatogram. The analyst must demonstrate acceptable performance, that is, precision and accuracy as defined in Section 10.3.

8.4.1 Establish HPLC operating conditions recommended in Section 9.2.1.

Calibrate the system daily as described in Section 9.2.4. Before each analysis check the detector baseline to ensure stable operation.

8.4.2 Draw a 100-uL aliquot of the sample into a clean HPLC injection syringe. Inject the sample after the sample injection loop (25 uL) is loaded. The first sample to be analyzed must be a quality control standard. Use the same size loop for quality control and calibration standards and unknown samples.

Alternatively, an automated constant volume injection system may also be used. The data system, if used must be activated simultaneously with the injection, and the point of injection marked on the strip chart recorder.

8.4.3 After allowing sufficient operating time to displace all of the sample out of the loop and onto the column, return the injection valve to the "load" position so that the sample loading operation can be repeated.

Rinse or flush the syringe and valve in preparation for the next sample analysis.

8.4.4 After elution of the DNPH-formaldehyde derivative (Figure 5), terminate data acquisition and calculate the component concentrations as described in Section 11.

8.4.5 Allow the detector baseline to stabilize before analyzing the next sample. After a stable baseline is achieved, the system may be used for further sample analyses as described above.

(Note: After several sample analyses, buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.)

8.4.6 If the concentration of analyte exceeds the linear range of the instrument, dilute the sample with mobile phase (6.3.4), or inject a smaller volume into the HPLC.

8.4.7 Compare the retention time(s) of the peak(s) in the sample chromatogram with those of the peaks in the standard chromatograms. The width of the retention time window used to make identifications must be based upon measurements of actual retention time variations of standards over the course of a day.
If the retention time is not duplicated (±10%), as determined by the calibration curve, increase or decrease the acetonitrile/water ratio, as necessary, to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

(NOTE: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.)

9. CALIBRATION

Maintain a laboratory log of all calibrations.

9.1 Sampling

9.1.1 Dry Gas Meter: Before and after each use in the field, calibrate the dry gas meter with a NBS traceable standard meter.
If the calibration factors obtained before and after a test differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever factor gives the lower value of total sample volume.

9.1.2 Flow Meter: Before use in the field, calibrate with a flow meter calibrator which has been calibrated with a primary flow calibrator that is NBS traceable. Choose a flow meter such that the flow rate to be used in the field is in the linear range of the calibration curve.

After each field use, check the calibration. If the calibration factors obtained before and after a test differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever factor gives the lower value of total sample volume.

9.2 Analytical

9.2.1 The HPLC system is assembled as shown in Figure 6. The following operating conditions are recommended. Other columns, chromatographic conditions, or detectors may be used if the conditions of Section 10.3 are met.

The chromatographic conditions described here have been optimized for a gradient HPLC (Varian Model 5000) system equipped with a UV detector (ISCO Model 1840 variable wavelength), an automatic sampler with a 25-uL loop injector and a BondaPak C-18 (3.9mm x 30 cm) column, a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs.

9.2.1.1 Column: Bondapak C-18 (3.9 mm ID x 30 cm), or equivalent.

9.2.1.2 Mobile Phase: 60% acetonitrile/40% water, isocratic (9.2.2).

9.2.1.3 Detector: Model 490 UV/Vis operating at 360 nm. Sample rate 1 point/sec and 1.00 absorbance units full scale (AUFS).

9.2.1.4 Flow Rate: 1.0 mL/min.

9.2.1.5 Run Time: 25 minutes

9.2.1.6 Retention Time: Approximately 13.5 minutes for formaldehyde

9.2.1.7 Injection Volume: 25 uL.

9.2.2 The HPLC mobile phase is prepared by mixing 600 mL of acetontrile and 400 mL of water. This mixture is filtered

through a 0.22-um polyester membrane filter in an all-glass and Teflon suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/minute) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or short length (15-30 cm) of 0.25 mm (0.01 inch) I.D. Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

9.2.3 The mobile phase is placed in the HPLC solvent reservior and the pump is set at a flow rate of 1.0 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device at a sensitivity of 1.00 AUFS. Once a stable baseline has been achieved, the system is ready for calibration.

9.2.4 Inject a minimum of 5 calibration standards (7.3.2) using the same technique that will be used to introduce samples into the HPLC (8.4.2). Analyze each calibration standard according to Section 8.4. The retention times of the analyte must agree within 2%. Tabulate peak height or area responses against the mass injected. Use the results to prepare a calibration curve as illustrated in Figure 4. A linear response range of approximately 0.05 to 10 mg/L should be achieved for 25 uL injection volumes. Linearity through the origin is assumed if a correlation coefficient of at least 0.999 is obtained for a linear least squares fit of the data.

9.2.5 The average response factor may be used in place of a calibration curve if linear response has been documented. One or more daily calibration standards may be used to verify the working calibration curve or response factor. For such verification use intermediate concentration standards near the anticipated levels of the analyte but at least 10 times the detection limit. Use the response for the daily calibration standard to calculate a response factor (RF) according to equation 11-5. The daily RF for the analyte should not vary from the predicted RF by more than 10%. If greater variability is observed, recalibrate or develop a new calibration curve from fresh standards.

9.2.6 Check the calibration of the instrument for each run (20 or fewer samples) by analyzing a control sample. The concentration given must fall within the UCL and LCL of the control sample value (10.4).

10. QUALITY ASSURANCE/QUALITY CONTROL

10.1 Sampling

10.1.1 Field Blanks: At least two impingers in each series of test runs shall be field blanks. These blanks should consist of materials that are used for sample collection, and must be handled with exactly the same procedures as the samples.

10.1.2 Blank Train: At least one sampling train in each series of test runs shall be a blank train. Prepare and set up the blank impinger train as described in Section 8.1 for the sampling trains. The blank train shall be taken through all of the steps from preparation to leak check without actually drawing sample gas through train. Instead, flush with nitrogen (6.1.6) for the same length of time as a single test run. Recover the blank train as described in Sections 8.2 and 8.3 for sampling trains.

10.1.3 Field Spikes: There must be at least one field spike per series of test runs. In cases where samples are taken before and after air pollution control equipment, there must be field spikes for each location. A field spike shall consist of a vial of impinger solution spiked with a known amount of DNPH-formaldehyde, and transported to the sampling location where it remains for the duration of a single test run. The appropriate spike level will depend on the source to be tested. The spiked samples must be carried through all of the required steps for sample preparation and analysis.

10.2 Analytical

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (according to Section 10.3), and the ongoing analysis of spiked samples as a continuing check on performance.

The laboratory must maintain performance records to document the quality of data that are generated. The laboratory must compare the results of their ongoing data quality checks with established performance criteria (10.3) to determine if the results of the analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard (10.3.2) must be analyzed to determine whether the instrument was operating within the control limits.

In recognition of the rapid advances occuring in HPLC the analyst is permitted options to improve separations. Such modifications are subject to approval by the Executive Officer. The analyst must

also produce data to demonstrate that the method meets the requirements of Sections 10.3 and 10.4 below.

10.2.1 Contamination Checks: Before processing any field samples, the analyst must demonstrate, through analysis of a method blank (10.2.2) that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a method blank must be processed as a safeguard against chronic laboratory contamination.

10.2.2 Laboratory Method Blank: The analyst must run a laboratory method blank along with each set of samples (20 or fewer). A method blank is prepared for analysis by executing all of the specified extraction steps (8.3) except for the introduction of sample.

10.2.3 Laboratory Spikes: The laboratory must on an ongoing basis spike, with standard stock solution (7.3), at least one sample per analytical batch of 20 or fewer samples to assess the accuracy of the analytical procedure. The formaldehyde concentration of the DNPH-formaldehyde spike should be :

(1) the regulatory concentration limit if the analyte is being checked against such a limit, or,

(2) the larger of either 5 times higher than the background concentration, or the QC check sample concentration (Section 10.3.2).

Determine the percent recovery of the spikes using equation 11-1.

10.3 Quality Control Check Samples

As an initial demonstration of acceptable performance, the laboratory must document the ability to generate acceptable accuracy and precision with this method, using a laboratory control standard.

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following.

10.3.1 Select a representative concentration. Use a stock standard prepared independently from those used for calibration to prepare a concentrated quality (QC) check sample with mobile phase (6.3.4) as the solvent. The concentration of DNPH-formaldehyde should be 100 times greater than the representative concentration selected above.

10.3.2 Prepare QC check samples by pipetting 1.00 mL of the QC check sample concentrate (10.3.1) into each of four 100-mL aliquots of mobile phase.

10.3.3 Analyze the well-mixed QC check sample according to Sections 8.3 and 8.4 beginning with the extraction of the samples.

10.3.4 Calculate the average percent recovery (R) using equation 11-1, and the standard deviation (s) of the four recovery measurements.

10.3.5 Compare s and R with the acceptance criteria for precision and accuracy determined in Section 10.4. If R and s meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If s exceeds the precision limit or R falls outside the range for accuracy, then the system performance is unacceptable. In that case, the analyst must locate and correct the source of the problem and repeat the process beginning with Section 10.3.

10.4 Method Precision and Accuracy:

10.4.1 Precision of response to replicate HPLC injections must be ±10% or less, day to day, for calibration standards. Precision of retention times must be ±10% or less, day to day, for calibration standards. Precision of retention times must be ±2% on a given day.

10.4.2 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration of analyte being measured.

Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = R + 2 s
Lower Control Limit (LCL) = R - 2 s

where R and s are as defined in Section 10.3.4. The UCL and LCL can be used to construct control charts that can be used to follow trends in performance.

10.5 Standard Operating Procedures (SOP's)

10.5.1 Users must generate SOPs describing the following activities in their laboratory:

(1) assembly, calibration, and operation of the sampling system, with make and model of equipment used;

(2) preparation, purification, storage, and handling of sampling reagent and samples;

(3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and

(4) all aspects of data recording and processing, including lists of computer hardware and software used.

10.5.2 SOPs must provide specific stepwise instruction and should be readily available to and understood by the laboratory personnel conducting the work.

10.6 HPLC System Performance

10.6.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 6.

10.6.2 Determine the HPLC peak asymmetry factor and system efficiency in the following manner:
Inject a solution of DNPH-formaldehyde derivative corresponding to at least 20 times the detection limit, with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. Determine the peak asymmetry factor as shown in Figure 6. This should be between 0.8 and 1.8.

10.6.3 Calculate the HPLC system efficiency according to the following equation:

$$N = 5.54 \, (t_r/W_{1/2})^2$$

Where:

N = Column efficiency (theoretical plates)

t_r = Retention time (seconds) of the analyte

$W_{1/2}$ = width of peak of the analyte at half height (seconds)

A column efficiency of >5,000 theoretical plates should be obtained.

11. CALCULATIONS

11.1 Nomenclature

C_f - Concentration of HCHO in the stack gas (ng/dscm), dry basis, corrected to standard conditions of 760 mm Hg and 293 °K (528°R).

C_s - Concentration of HCHO in the stack gas (ppbv), dry basis corrected to standard conditions of 760 mm Hg and 293°K.

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

P_{std} - Standard absolute pressure (760 mmHg).

Q_A - Average sample flow rate (mL/min).

R - Recovery of QC check sample and spikes (%).

RF - Response Factor calculated according to Equation 11-5: the ratio of the amount of analyte injected in the calibration standard to the response (usually area counts) (ng injected/response unit)

V_E - Final volume of extract (mL) after dilution (from Section 8.4.6).

V_I - Volume of extract injected onto the HPLC system

$V_{m(std)}$ - Total sample volume (dscm) at standard conditions of 760 mmHg and 293°K.

W_d - Total quantity of formaldehyde-DNPH derivative in the sample (ug)

11.2 Percent Recovery, (R)

$$R = \frac{\text{Measured concentration (mg/L)}}{\text{Known concentration (mg/L)}} \times 100 \qquad \text{Equation 11-1}$$

11.3 Average Sample Flow Rate, Q_A, (mL/min)

If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate (Q_A) must be calculated according to equation 11-2.

$$Q_A = \frac{Q_1 + Q_2 + \ldots + Q_N}{N} \qquad \text{Equation 11-2}$$

Where:

$Q \ldots Q_N$ = flow rates measured during the sampling period, mL/min

N = number of flow rate measurements made

11.4 Total Volumetric Flow, V_m, (dcm)

Calculate the total volumetric flow (V_m) using equation 11-3.

$$V_m = \frac{(T_2 - T_1) \times Q_A}{10^6} \qquad \text{Equation 11-3}$$

Where:

V_m = total volume (dcm) sampled at the measured temperature and pressure

T_2 = stop time, min

T_2 = start time, min

Q_A = average flow rate, mL/min

11.5 Total Sample Volume at Standard Conditions, $V_{m(std)}$, (dscm)

Use Equation 11-4 to correct the sample volume to standard conditions, 20°C and 760 mm Hg).

$$V_{m(std)} = V_m \times \frac{293}{273 + t_A} \times \frac{P_{bar}}{P_{std}} \qquad \text{Equation 11-4}$$

Where:

t_A = temperature of the dry gas entering the flow meter (°C)

P_{bar} = barometric pressure at the sampling site, mm Hg

11.6 Response Factor, RF

Calculate the response factor (RF) using equation 11-5 and the data obtained in Section 8.4 from the analysis of the calibration standards.

$$RF = \frac{C_c \times V_i}{A_c} \qquad \text{Equation 11-5}$$

Where:

C_c = concentration (mg/L) of analyte in the daily calibration standard

A_c = Response (area counts) for the analyte in the calibration standard

V_i = Injected volume (µL) of calibration standard

11.7 Concentrations

11.7.1 Total DNPH-Formaldehyde Derivative in Sample, W_d, (µg): Use the following equation to calculate the total mass (µg) of DNPH-formaldehyde in the sample volume:

$$W_d = RF \times A_s \times \frac{V_E}{V_i} \qquad \text{Equation 11-6}$$

Where:

A_s = Response (area counts) for the analyte in the sample.

11.7.2 Mass concentration of Formaldehyde in Stack Gas, C_f, (ng/dscm): Use the following equation to calculate the total concentration of HCHO (ng/dscm) in the sample.

$$C_f = \frac{W_d}{V_{m(std)}} \times 1000 \times \frac{30}{210} \qquad \text{Equation 11-7}$$

Where:

30 = Molecular weight of formaldehyde (g/gmole).

210 = Molecular weight of DNPH-formaldehyde derivative (g/gmole).

11.7.3 Volumetric concentration of formaldehyde in stack gas, C_s, (ppbv): Use the following equation to calculate the total concentration of HCHO (ppbv) in the sample.

$$C_s = C_f \times \frac{24.05}{30} \times 10^3 \qquad \text{Equation 11-8}$$

Where:

30 = Molecular weight of formaldehyde (g/g mole).

24.05 = RuT/P, L/g mole at 293°K and 1 atm.

Where:

Ru = 0.08205 atm. L/°K g mole

T = 293°K

P = 1 atm.

12. ALTERNATIVE TEST METHODS FOR FORMALDEHYDE

The Executive Officer may approve an alternative test method, provided the Executive Officer finds the alternative test method to be equivalent to Test Method 430. To make this finding, the Executive Officer may require the person requesting the approval of the alternative test method to submit information needed to support the finding.

13. REFERENCES

13.1 ARB/SS-88-02. Formaldehyde: a candidate toxic air contaminant. March, 1988. CARB. Prepared by Barbara Fry and Tom Parker.

13.2 Method TO5. Method for the determination of aldehydes and ketones in ambient air using high performance liquid chromatography (HPLC). In "Compendium of methods for the determination of toxic organic compounds in ambient air" EPA-600/4-84-041. April 1984.

13.3 Method TO11. Method for the determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC). In "Compendium of methods for the determination of toxic organic compounds in ambient air" EPA-600/4-84-041. December, 1986.

13.4 Southern Research Institute. Development of analytical methods for ambient monitoring and source testing for toxic organic compounds. Volume I. Literature Review. Project 5614. California Air Resources Board. October 31, 1986.

13.5 Southern Research Institute. Development of analytical methods for ambient monitoring and source testing for toxic organic compounds. Volume II. Experimental Studies. Project 5614. California Air Resources Board. October 31, 1986.

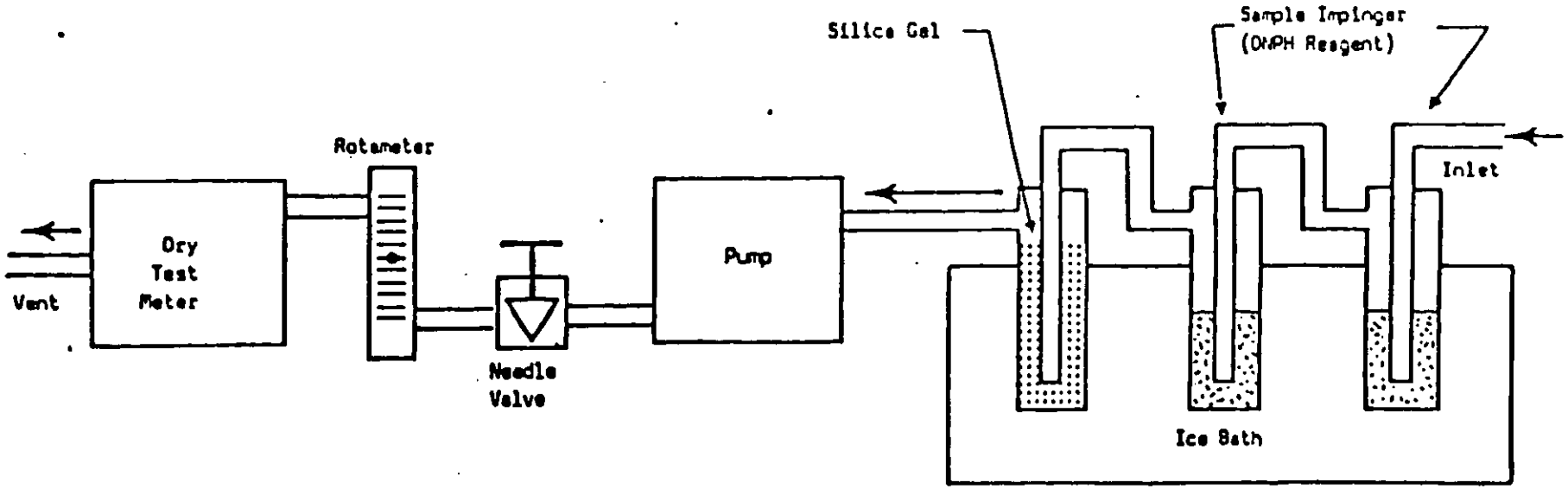


FIGURE 1. TYPICAL SAMPLING SYSTEM (13.2)

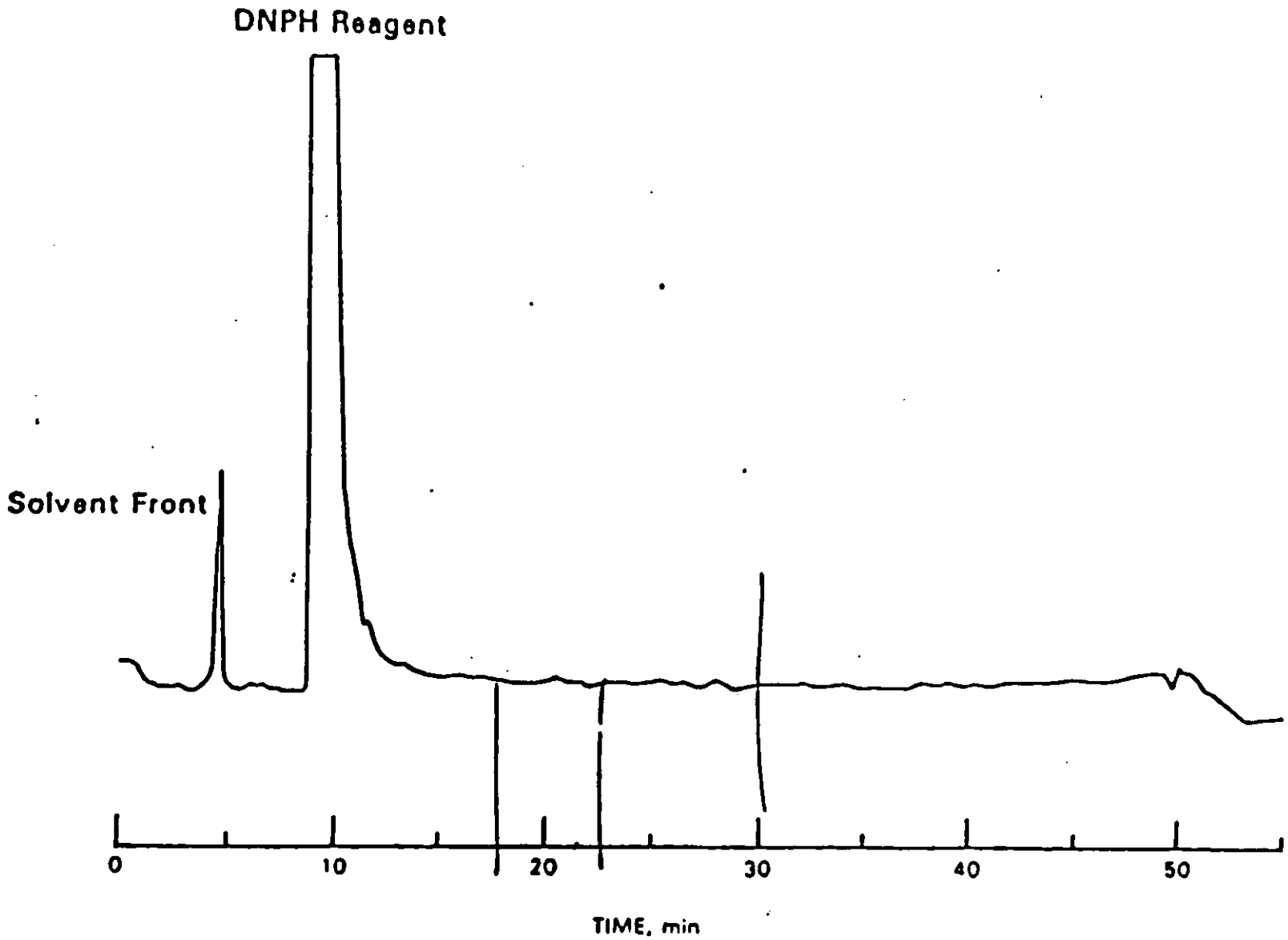


FIGURE 2. IMPURITY LEVEL OF DNPH AFTER RECRYSTALLIZATION (13.3)

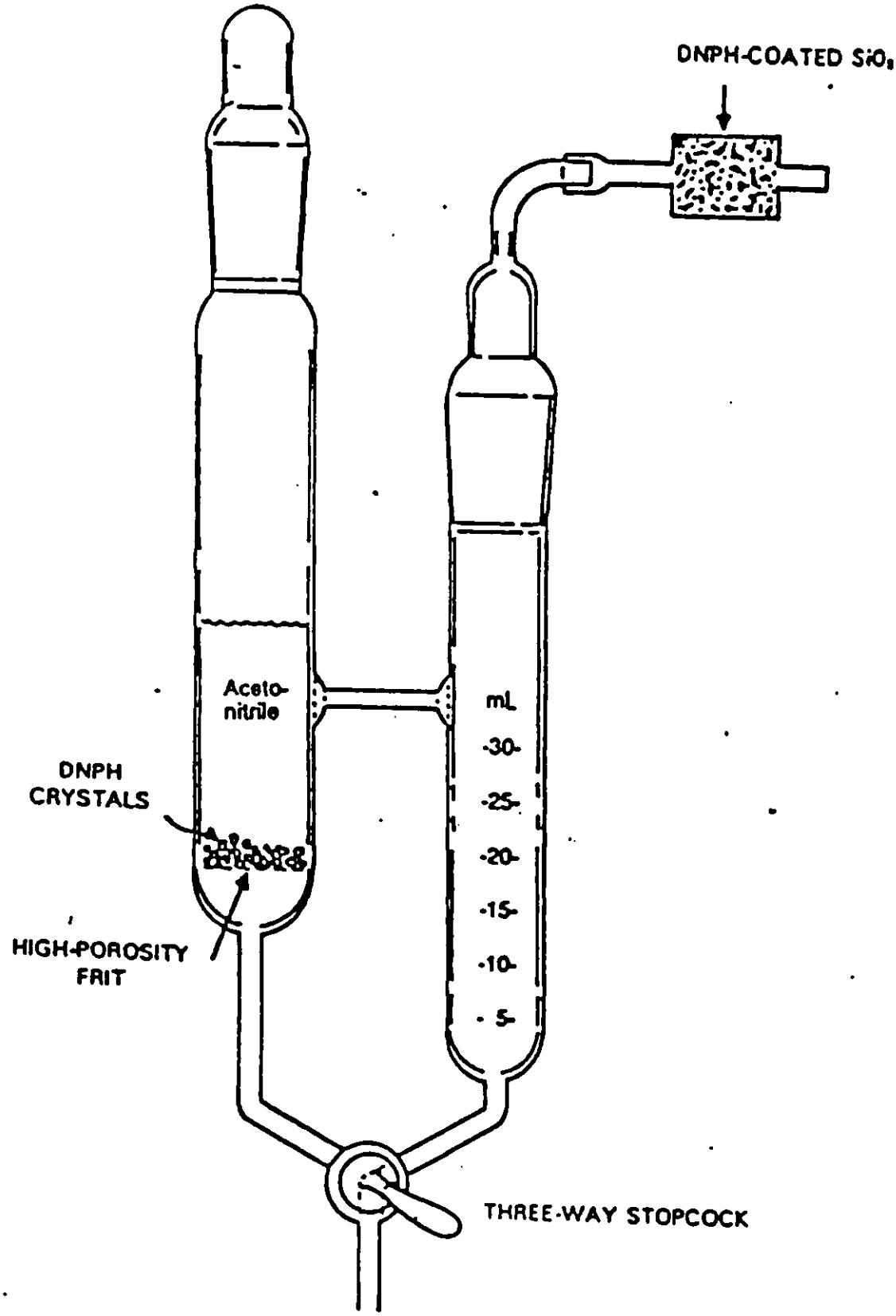


FIGURE 3. SPECIAL GLASS APPARATUS FOR RINSING, STORING, AND DISPENSING SATURATED DNPH STOCK SOLUTION (13.3)

FIGURE 4

SAMPLING DATA SHEET

(One Sample Per Data Sheet)

Run No: _____ Project No: _____

Location: _____ Plant Name: _____

Date Sampled: _____ Ambient Temp °F: _____

Time Period Sampled: _____ Bar. Press, in. Hg: _____

Operator: _____ Moisture, %: _____

SAMPLING DATA

Start Time: _____ Stop Time: _____

	Clock Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate, Q mL/min	Impinger Temp. °F	Stack Temp. °F	COMMENTS
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							

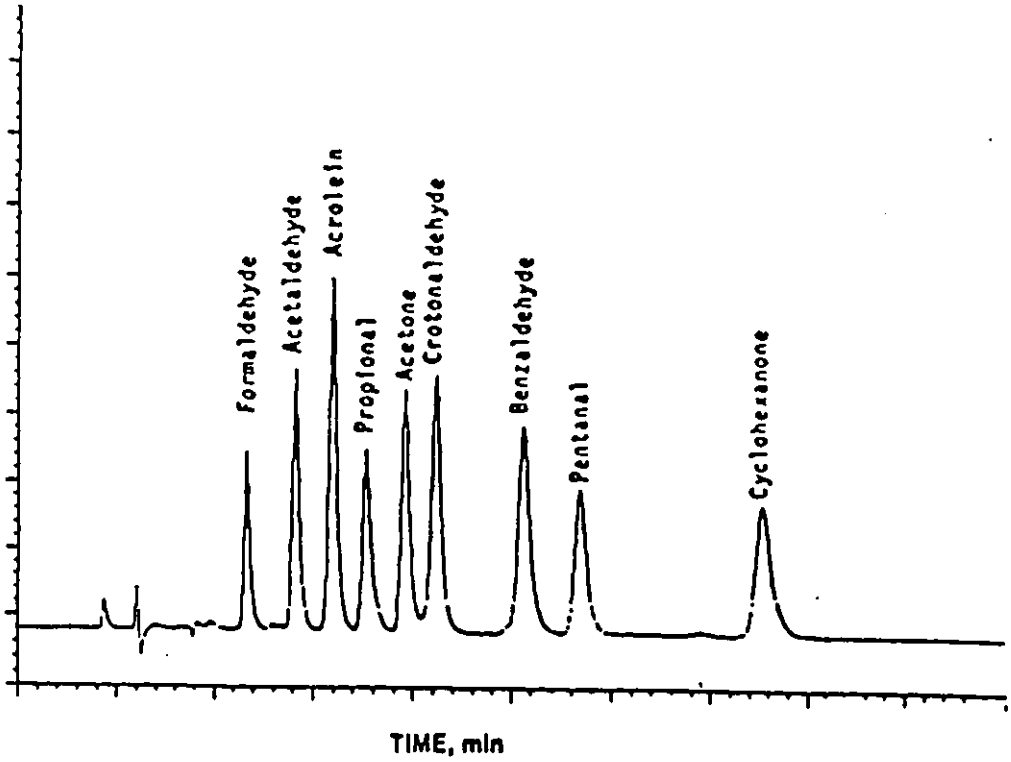


FIGURE 5A. TYPICAL HPLC CHROMATOGRAM (13.2)

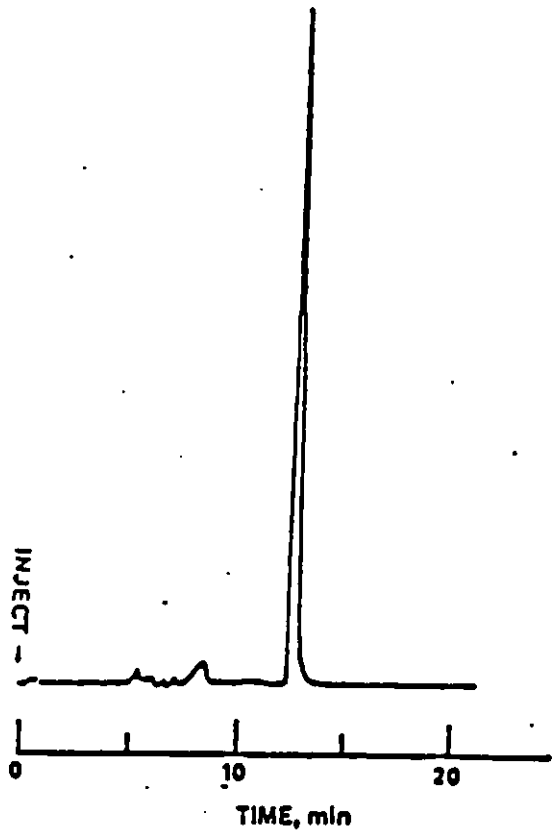


FIGURE 5B. CHROMATOGRAM OF DNPH–FORMALDEHYDE DERIVATIVE (13.3)

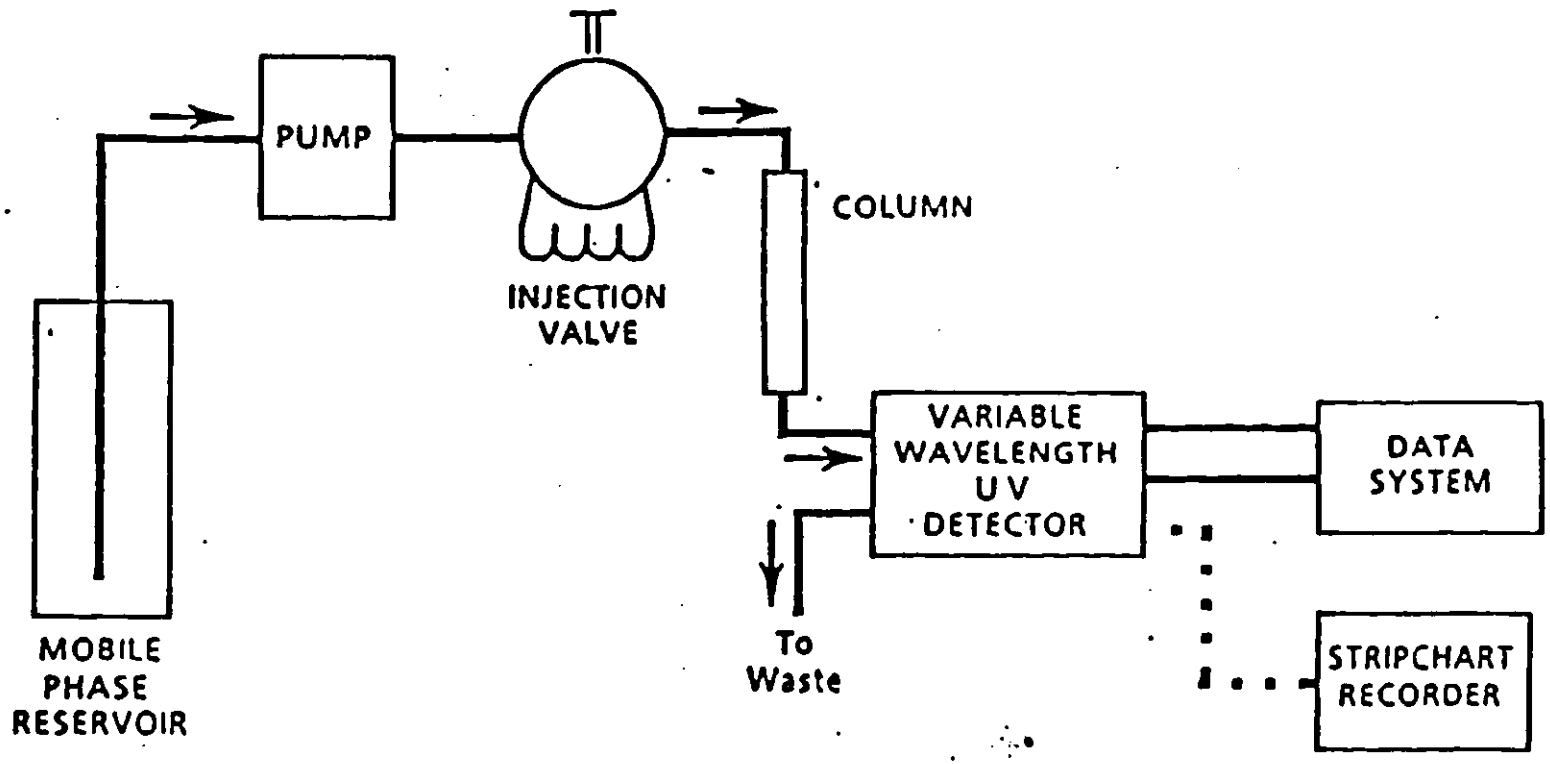
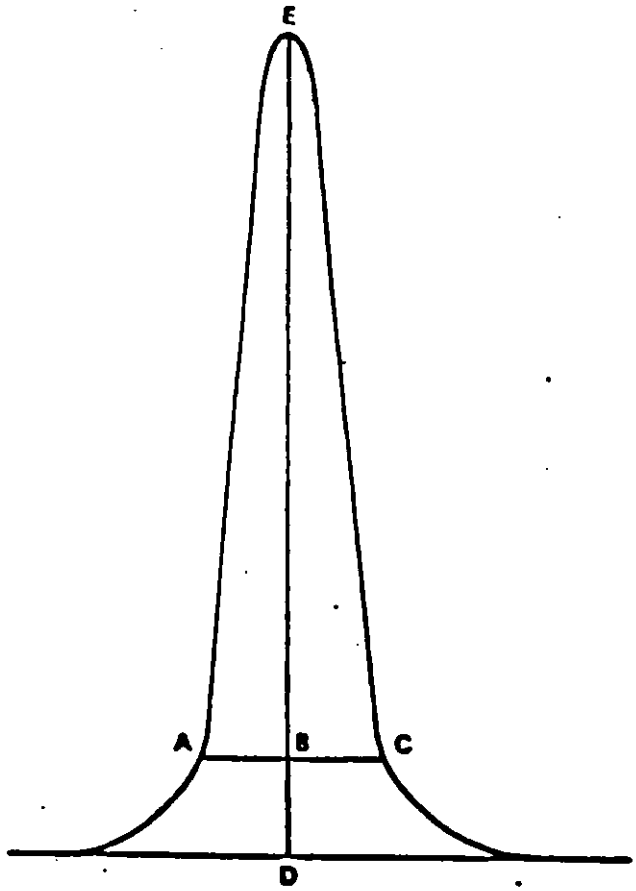


FIGURE 6. TYPICAL HPLC SYSTEM (13.2)



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Asymmetry Factor} = \frac{12}{11} = 1.1$$

FIGURE 7. PEAK ASYMMETRY CALCULATION (13.2)

APPENDIX N

USEPA

Draft Multiple Metals Method

EPA DRAFT MULTIPLE METALS METHOD

DRAFT 8/28/89

METHODOLOGY FOR THE DETERMINATION OF METALS EMISSIONS IN EXHAUST GASES FROM HAZARDOUS WASTE INCINERATION AND SIMILAR COMBUSTION PROCESSES

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the additional procedures described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front half mercury determination.*

1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing a solution of dilute nitric acid in hydrogen peroxide in two impingers, and acidic potassium permanganate solution in two (or one) impingers. Sampling train components are recovered and digested in separate front and back half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr® Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). Except for the permanganate solution, the remainder of the sampling

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*Field tests to date have shown that of the total amount of mercury measured by the method, only 0 to <2% was measured in the front half. Therefore, it is tentatively concluded, based on the above data, that particulate emissions may be measured by this train, without significantly altering the mercury results.

train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample fraction can be combined proportionally for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals including actual sample matrix effects checks.

2. Range, Sensitivity, Precision, and Interferences

2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (ug/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 ug/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 ug/ml of cadmium should be diluted to that level before analysis.

2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Ti (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the

following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (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 limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit, ug/ml.
B = volume of sample prior to aliquot for analysis, ml.
C = stack sample volume, dscm (dsm^3).
D = in-stack detection limit, ug/m^3.

Values in Table A-1 are calculated for the front and back half and/or the total train.

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. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition should be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A-1 for a specific test by using one or more of the following options:

- A normal 1-hour sampling run collects a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased and 5 m^3 are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (this means that with this change, the method is four times more sensitive than normal).
- 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 and 150 ml for the

TABLE A-1. IN-STACK METHOD DETECTION LIMITS (ug/m^3)
FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front Half Fraction 1 Probe and Filter	Back Half$_1$ Fraction 2 Impingers 1-3	Back Half$_2$ Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.05**	0.03**	0.03**	0.11**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

( )* Detection limit when analyzed by GFAAS.
** Detection limit when analyzed by CVAAS.
Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

back half sample. If the front half volume is reduced from 300 ml to 30 ml, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. A volume less than 25 ml may not allow resolubilization of the residue and may increase interference by other compounds.

- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase limits. The front half and back half, samples (Fractions 1 and 2) can be combined prior to analysis. The resultant liquid volume (excluding Fraction 3, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of Fraction 3 must be considered.
- The above discussion assumes no blank correction. Blank corrections are discussed later in this method.

2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Refer to EPA Method 6010 (SW-846) for details on potential interferences for this method. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure A-1. It is similar to the Method 5 train. The sampling train consists of the following components.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2. Glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or

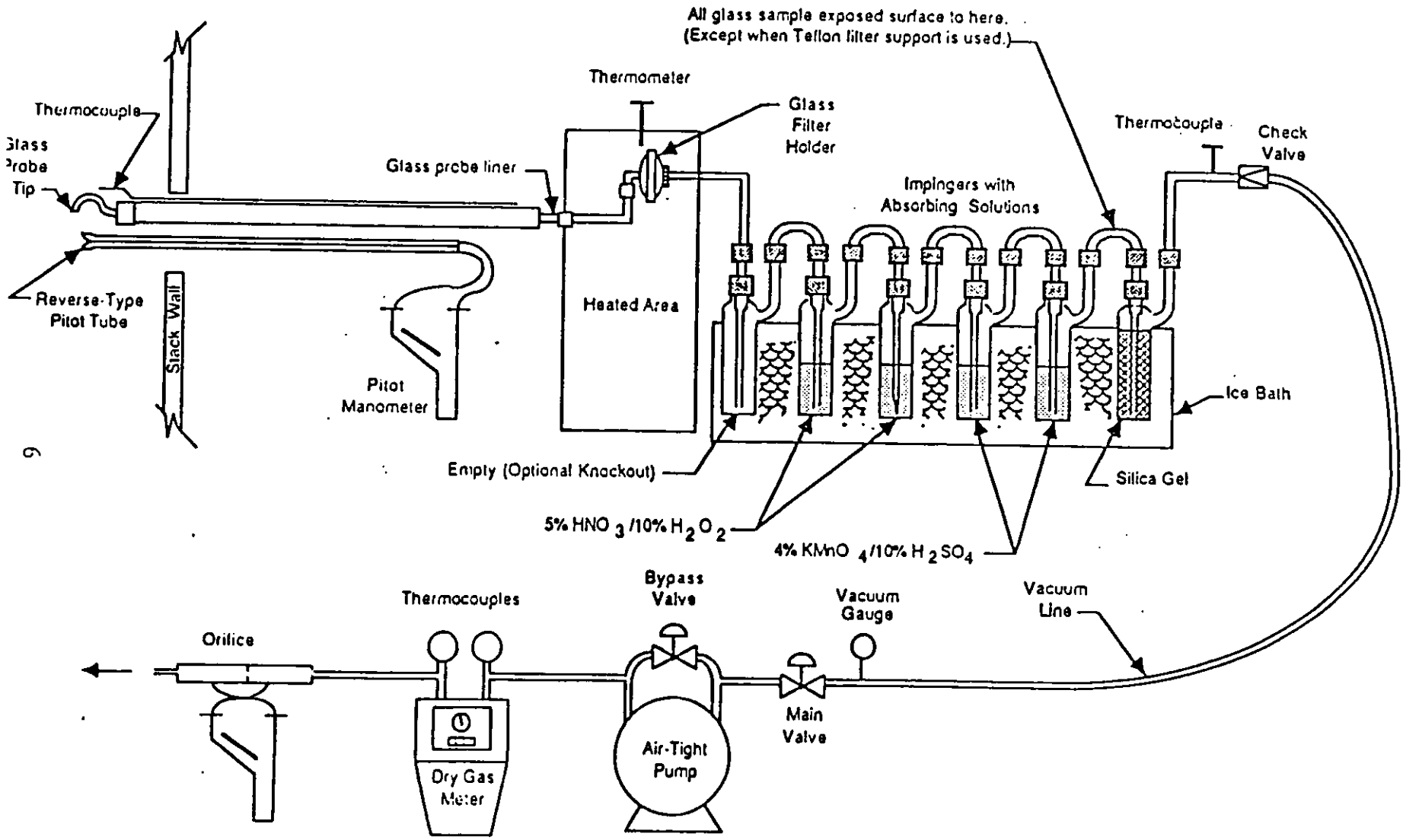


Figure A-1. Schematic of multiple metals sampling train.

interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except that a Teflon filter support must be used to replace the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to six impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a water knockout trap for use during test conditions which require such a trap. The impingers to be used in the metals train are now described. When the first impinger is used as a water knockout, it shall be appropriately-sized for an expected large moisture catch and constructed generally as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first HNO_3/H_2O_2 impinger) shall also be as described for the first impinger in Method 5. The third impinger (or the impinger used as the second HNO_3/H_2O_2 impinger) shall be the same as the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the metals train are the same as the second impinger (the first HNO_3/H_2O_2 impinger) previously described in this paragraph. In summary, the first impinger should be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 4.2.1), the fourth (and fifth, if required) shall contain a known quantity of acidic potassium permanganate solution (Section 4.2.2), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers are removed.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.7 Teflon Tape. For capping openings and sealing connections on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps, 1000- and 500-ml, shall be used for $KMnO_4$-containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identification of samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100 ml, 250 ml, and 1000 ml. For preparation of standards and sample dilution.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr® Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).

3.3.4 Beakers and Watchglasses. 250 ml beakers for sample digestion with watchglasses to cover the tops.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.3.8 Disposable Pasteur Pipets and Bulbs.

3.3.9 Volumetric Pipets.

3.3.10 Analytical Balance. Accurate to within 0.1 mg.

3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.3.12 Hot Plates.

3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).

3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as EPA Method 7470.

3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

4. Reagents

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

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

4.1.1 Filters. The filters shall contain less than 1.3 ug/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended.

4.1.2 Water. To conform to ASTM Specification D1193-77, Type II (incorporated by reference). Analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

4.1.6 Potassium Permanganate.

4.1.7 Sulfuric Acid. Concentrated.

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

4.2 Pretest Preparation for Sampling Reagents.

4.2.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add 50 ml of concentrated HNO_3 and 333 ml of 30 percent H_2O_2 to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water. Dilute to volume with water. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.2 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V). Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.2.3 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.4 Hydrochloric Acid (HCl), 8 N. Add 690 ml of concentrated HCl to a graduated cylinder containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

4.3 Glassware Cleaning Reagents.

4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.3.3 Nitric Acid, 10 Percent (V/V). Add 500 ml of concentrated HNO_3 to a graduated cylinder containing approximately 4000 ml of water. Dilute to 5000 ml with water.

4.4 Sample Digestion and Analysis Reagents.

4.4.1 Hydrochloric Acid, Concentrated.

4.4.2 Hydrofluoric Acid, Concentrated.

4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.4.4 Nitric Acid, 10 Percent (V/V). Add 100 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.5 Nitric Acid, 5 Percent (V/V). Add 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 for preparation.

4.4.8 Stannous Chloride.

4.4.9 Potassium Permanganate, 5 Percent (W/V).

4.4.10 Sulfuric Acid, Concentrated.

4.4.11 Nitric Acid, 50 Percent (V/V).

4.4.12 Potassium Persulfate, 5 Percent (W/V).

4.4.13 Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$.

4.4.14 Lanthanum Oxide, La_2O_3.

4.4.15 AAS Grade Hg Standard, 1000 ug/ml.

4.4.16 AAS Grade Pb Standard, 1000 ug/ml.

4.4.17 AAS Grade As Standard, 1000 ug/ml.

4.4.18 AAS Grade Cd Standard, 1000 ug/ml.

4.4.19 AAS Grade Cr Standard, 1000 ug/ml.

4.4.20 AAS Grade Sb Standard, 1000 ug/ml.

4.4.21 AAS Grade Ba Standard, 1000 ug/ml.

4.4.22 AAS Grade Be Standard, 1000 ug/ml.

4.4.23 AAS Grade Cu Standard, 1000 ug/ml.

4.4.24 AAS Grade Mn Standard, 1000 ug/ml.

4.4.25 AAS Grade Ni Standard, 1000 ug/ml.

4.4.26 AAS Grade P Standard, 1000 ug/ml.

4.4.27 AAS Grade Se Standard, 1000 ug/ml.

4.4.28 AAS Grade Ag Standard, 1000 ug/ml.

4.4.29 AAS Grade Tl Standard, 1000 ug/ml.

4.4.30 AAS Grade Zn Standard, 1000 ug/ml.

4.4.31 AAS Grade Al Standard, 1000 ug/ml.

4.4.32 AAS Grade Fe Standard, 1000 ug/ml.

4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA Method 7470 or Standard Methods for the Analysis of Water and Wastewater. 15th Edition, Method 303F should be referred to for additional information on mercury standards.

4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 ug/ml intermediate mercury standard by adding 5 ml of 1000 ug/ml mercury stock solution to a 500 ml volumetric flask; dilute to 500 ml by first adding 20 ml of 15 percent HNO_3 and then adding water. Prepare a working mercury standard solution fresh daily: add 5 ml of the 10 ug/ml intermediate standard to a 250 ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until in the range of the calibration.

4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 ug/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a

separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 50 ug/ml for Al, 25 ug/ml for Cr and Pb, 15 ug/ml for Fe, and 10 ug/ml for the remaining elements. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Lead, Selenium, and Thallium. Prepare a 10 ug/ml standard by adding 1 ml of 1000 ug/ml standard to a 100 ml volumetric flask. Dilute to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/ml standard by adding 1 ml of the 10 ug/ml standard to a 100 ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.37 Matrix Modifiers.

4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_2O$ in approximately 50 ml of water in a 100 ml volumetric flask. Dilute to 100 ml with water.

4.4.37.2 Nickel Nitrate, One-tenth Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

4.4.37.3 Lanthanum. Dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3 and dilute to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

5. Procedure

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

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 4.2.1) in the two HNO_3/H_2O_2 impingers (normally the second and third impingers), place 100 ml of the acidic potassium permanganate solution (Section 4.2.2) in the fourth and fifth impinger, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 150 ml. The tester shall include two impingers containing the acidic potassium permanganate solution for the first test run, unless past testing experience at the same or similar sources has shown that only one is necessary. The last permanganate impinger may be discarded if both permanganate impingers have retained their original deep purple permanganate color. A maximum of 200 ml in each permanganate impinger (and a maximum of three permanganate impingers) may be used, if necessary, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks, 100 ml of the nitric acid/hydrogen peroxide solution and 100 ml of the acidic potassium permanganate solution. These solutions should be labeled and treated as described in Section 7. Set up the sampling train as shown in Figure A-1. If necessary to ensure leak-free sampling train connections, Teflon tape should be used instead of silicone grease to prevent contamination.

Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

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

5.2 Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination

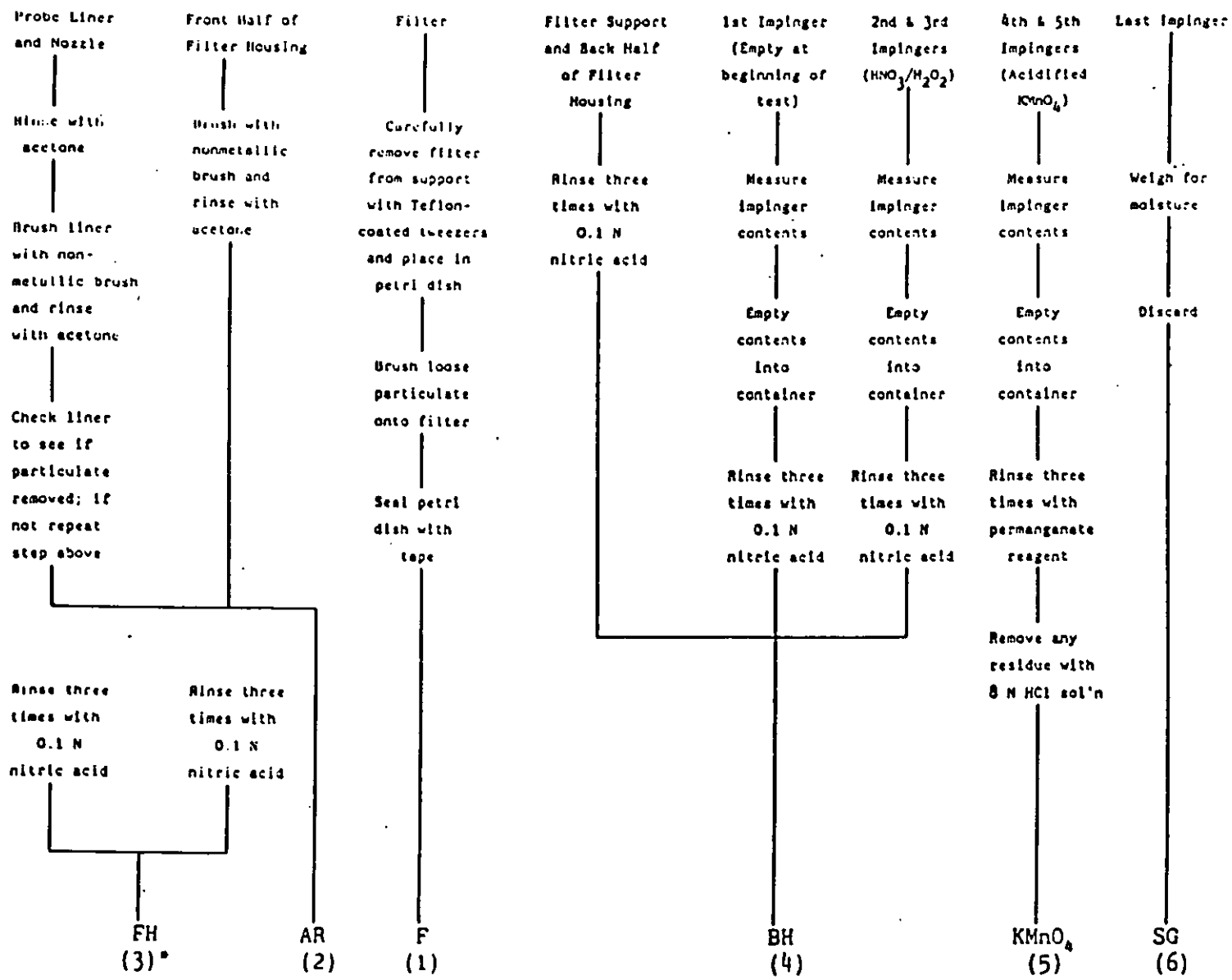
or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure A-2). Assure that all items necessary for recovery of the sample do not contaminate it.

5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.2 Container No. 2 (Acetone Rinse). Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

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

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample



* Number in parantheses indicates container number.

Figure A-2. Sample recovery scheme.

container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

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

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

5.2.3 Container No. 3 (Probe Rinse). Rinse the probe liner, probe nozzle, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

5.2.4 Container No. 4 (Impingers 1 through 3, Contents and Rinses). Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid as

described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Calculate the 0.1 N nitric acid rinse volume by difference. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 4 & 5). Pour all the liquid from the permanganate impingers (fourth and fifth, if two permanganate impingers are used) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Using 100 ml total of the acidified potassium permanganate solution, rinse the permanganate impinger(s) and connecting glass pieces a minimum of three times. Combine the rinses with the permanganate impinger solution. Finally, rinse the permanganate impinger(s) and connecting glassware with 50 ml of 8 N HCl to remove any residue. Note: The use of exactly 100 ml and 50 ml for the two rinses is necessary for the subsequent blank correction procedures. Place the combined rinses and impinger contents in a labeled glass storage bottle. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.2.2 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

5.2.6 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. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.

Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.7 Container No. 7 (Acetone Blank). Once during each field test, place 100 ml 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.

5.2.8 Container No. 8 (0.1 N Nitric Acid Blank). Once during each field test, place 200 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front half and back half field reagent blanks. Seal the container.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). 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.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). Once during each field test, place 300 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container.

Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Blank). Once during each field test, place 50 ml of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into a labeled container for use in the back half reagent blank for mercury.

5.2.12 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.

5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure A-3.

5.3.1 Container No. 1 (Filter). If particulatre emissions are being determined, then desiccate the filter and filter catch without heat and weigh to

a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr[R] Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.3, below.

Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to an acid-cleaned tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Resolubilize the residue with concentrated nitric acid and combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 50 ml by heating on a hot plate at a temperature

just below boiling. Inspect the sample for visible particulate matter, and depending on the results of the inspection, perform one of the following. If no particulate matter is observed, combine the sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. If particulate matter is observed, digest the sample in microwave vessels or Parr[R] Bombs following the procedures described in Section 5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50 ml aliquot and label as Fraction 1B. Label the remaining 250 ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 50 ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as Fraction 2A. The Fraction 2B aliquot should be prepared and analyzed as described in Section 5.4.3. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes.

Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

5.3.5 Container No. 5 (Impingers 4 & 5). Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction 3. Follow the analysis procedures described in Section 5.4.3.

5.3.6 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.)

5.4 Sample Analysis. For each sampling train, five individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure A-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front half mercury as described in Section 5.4.3.

The back half of the train was used to prepare the third through fifth samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the H_2O and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth sample, labeled Fraction 3, consists of the impinger contents and rinses from the permanganate Impingers 4 and 5. This sample is analyzed for mercury as described in Section 5.4.3. The total back half mercury catch is determined from the sum of Fraction 2B and Fraction 3.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 200.7. The quality control procedures described in Section 7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below.

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the target metals plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic and lead.

Note: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front half samples will contain hydrofluoric acid, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table A-2 should be used to determine which techniques and methods should be applied for each target metal. Table A-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fraction 3 should be analyzed for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up

TABLE A-2. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTEFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelenght of 231.1 nm. Match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volati - zation Aluminium	Spiked samples & add nickel nitrate solution to digestates prior to analyses Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg & Si	Add 0.1% floyride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to miminize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scatt	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a know constant effect and to eliminate effect of phosphate

(continued)

TABLE A-2 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference Cause	Interference Minimization
Cu	Aspiration	7210	324.7	Absorpt & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care taken to aviod contamination
Pb	Aspiration	7420	283.3	217.0 nm alternat	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorus acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternat	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternat Fe, Co, & Cr Nonlinear respons	Background correction required Matrix matching or a nitrous-oxide/acety flame Sample dilution or use 352.4 nm line
Se	Furnace	7740	196.0	Volitality Adsorpt & scatter	Spike samples & reference materials & add nickel nitrate to minimize volatilization Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt & scatter AgCl insoluble Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample & standards monitored for apiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occuring for volitization by spiked samples or standad addt Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Strontium removes Cu and phosphate Care should be taken to avid contamination

the calibration curve as described in Section 7.3 of Method 303F. Add approximately 5 ml of each sample to BOD bottles. Record the amount of sample added. The amount used is dependent upon the expected levels of mercury. Dilute to approximately 120 ml with mercury-free water. Add approximately 15 ml of 5 percent potassium permanganate solution to the Fraction 2B and Fraction 3 samples. Add 5 percent potassium permanganate solution to the Fraction 1B sample as needed to produce a purple solution lasting at least 15 minutes. A minimum of 25 ml is suggested. Add 5 ml of 50 percent nitric acid, 5 ml of concentrated sulfuric acid, and 9 ml of 5 percent potassium persulfate to each sample and each standard. Digest the solution in the capped BOD bottle at 95°C (205°F) in a convection oven or water bath for 2 hours. Cool. Add 5 ml of hydroxylamine hydrochloride solution and mix the sample. Then add 7 ml of stannous chloride to each sample and analyze immediately.

6. Calibration

Maintain a laboratory log of all calibrations.

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

6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.

6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table A-2 and in Standard Methods for Water and Wastewater, 15th Edition, Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

7. Quality Control

7.1 Sampling. Field Reagent Blanks. The blank samples in Container Numbers 7 through 12 produced previously in Sections 5.2.7 through 5.2.11, respectively, shall be processed, digested, and analyzed as follows. Digest and process Container No. 12 contents per Section 5.3.1, Container No. 7 per Section 5.3.2, and half of Container No. 8 per Section 5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. Combine the remaining half of Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.4. This produces Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. Container No. 10 and Container No. 11 contents are Fraction Blank 3. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 5.4.1 and/or 5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blank 3 per Section 5.4.3. The analysis of Fraction Blank 1A produces the front half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front half reagent blank correct value for mercury. The analysis of Fraction Blank 2A produces the back half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B and 3 produce the back half reagent blank correction value for mercury.

7.2 An attempt may be made to determine if the laboratory reagents used in Section 5.3 caused contamination. They should be analyzed by the procedures in Section 5.4. The Administrator will determine whether or not the laboratory blank reagent values can be used in the calculation of the stationary source test results.

7.3 Quality Control Samples. The following quality control samples should be analyzed.

7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 5% of average or repeat all analysis).

7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese,

Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc. All samples should be analyzed in duplicate. Perform a matrix spike on one front half sample and one back half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.

7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 10% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA Method 7470 or in Standard Methods for Water and Wastewater, 15th Edition, Method 303F.

8. Calculations

8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

8.4 Metals (Except Mercury) in Source Sample.

8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_s \; F_d \; V_{soln.1} \qquad \text{Eq. 1*}$$

*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

M_{fh} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), ug.

C_a = concentration of metal in sample Fraction 1A as read from the standard curve (ug/ml).

F_d = dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_a. For example, when the dilution of Fraction 1A is from 2 to 10 ml, F_d = 5).

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.

8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_a \; F_a \; V_a \qquad \text{Eq. 2*}$$

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), ug.

C_a = concentration of metal in sample Fraction 2A, as read from the standard curve (ug/ml).

F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A.

V_a = volume of digested sample analyzed (concentrated Fraction 2A), ml.

8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \qquad \text{Eq. 3*}$$

where:

M_t = total mass of each metal (separately stated for each metal) collected in the sampling train, ug.

M_{fhb} = blank correction value for mass of metal detected in front half field reagent blank, ug.

M_{bhb} = blank correction value for mass of metal detected in back half field reagent blank, ug.

*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

Note: If the measured blank value for the front half (m_{fhb}) is in the range 0.0 to A ug [where A ug equals the value determined by multiplying 1.4 ug per square inch (1.4 ug/in.^{2}) times the actual area in square inches (in.^{2}) of the filter used in the emission sample], m_{fhb} may be used to correct the emission sample value (m_{fh}); if m_{fhb} exceeds A ug, the greater of the two following values (either I. or II.) may be used:

I. A ug, or

II. the lesser of (a) m_{fhb}, or (b) 5 percent of m_{fh}.

If the measured blank value for the back half (m_{bhb}) is in the range 0.0 to 1 ug, m_{bhb} may be used to correct the emission sample value (m_{bh}); if m_{bhb} exceeds 1 ug, the greater of the two following values may be used: 1 ug or 5 percent of m_{bh}.

8.5 Mercury in Source Sample.

8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} \times V_{soln.1} \qquad \text{Eq. 4}$$

where:

Hg_{fh} = total mass of mercury collected in the front half of the sampling train (Fraction 1), ug.
Q_{fh} = quantity of mercury in analyzed sample, ug.
$V_{soln.1}$ = total volume of digested sample solution (Fraction 1), ml.
V_{f1B} = volume of Fraction 1B analyzed, ml. See the following Note.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100 ml dilution was analyzed, V_{f1B} would be 0.01.

8.5.2 Fraction 2B and Fraction 3, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 and 3 using Equations 5 and 6, respectively. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f1B}} \times V_{soln.2} \qquad \text{Eq. 5}$$

where:

Hg_{bh2} = total mass of mercury collected in Fraction 2, ug.
Q_{bh2} = quantity of mercury in analyzed sample, ug.
V_{f2B} = volume of Fraction 2B analyzed, ml (see Note in Section 8.5.1).
$V_{soln.2}$ = total volume of Fraction 2, ml.

$$Hg_{bh3} = \frac{Q_{bh3}}{V_{f2B}} \times V_{soln.3} \qquad \text{Eq. 6}$$

where:

Hg_{bh3} = total mass of mercury collected in Fraction 3, ug.
Q_{bh3} = quantity of mercury in analyzed sample, ug.
V_{f3} = volume of Fraction 3 analyzed, ml (see Note in Section 8.5.1).
$V_{soln.3}$ = total volume of Fraction 3, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3} \qquad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, ug.

8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$M_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 8}$$

where:

M_t = total mass of mercury collected in the sampling train, ug.
Hg_{fhb} = blank correction value for mass of mercury detected in front half field reagent blank, ug.
Hg_{bhb} = blank correction value for mass of mercury detected in back half field reagent blank, ug.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0 to 3 ug, then the total may be used to correct the emission sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 3 ug, the greater of the following two values may be used: 3 ug or 5 percent of the emission sample value ($Hg_{fh} + Hg_{bh}$).

8.6 Metal Concentration of Stack Gas. Calculate the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4 \ (M_t / V_{m(std)}) \qquad \text{Eq.9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.
K_4 = 10^{-3} mg/ug.
M_t = total mass of each metal collected in the sampling train, ug.
$V_{m(std)}$ = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

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

9. Bibliography

9.1 Method 303F in Standard Methods for the Examination of Water Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

9.2 EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

9.3 EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

9.4 EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1987.