Sampling Methods and Analytical Procedures Manual for PCB Disposal: Interim Report

February 10, 1978

PREPARED BY: J. Howard Beard, III
John Schaum
Office of Solid Waste
U.S. Environmental
Protection Agency
Washington, D.C. 20460

PREFACE

This manual is a compendium of sampling methods and analytical procedures which may be referred to and used by the PCB disposal facility owner/operators to assist them with any sampling and analytical testing which may be required under 40 CFR Part 761, Polychlorinated Biphenyls. However, due to the short time period in which this manual was prepared, the U.S. Environmental Protection Agency is issuing this manual as an interim document. (The U.S. EPA believes that a sampling methods and analytical procedures manual has to be available to PCB disposal facility owner/operators at the time the regulation is finally promulgated to successfully implement the site approval process under 40 CFR Part 761, Polychlorinated Biphenyls.) A final version of this manual is expected to be issued, after undergoing further review within the U.S. EPA, by early spring of 1978.

Table of Contents

Atachments

1.0 INTRODUCTION

1.1 Purpose

The purpose of this manual is to provide guidance to the PCB disposal facility owner/operators with any sampling methods and analytical procedures which may be required by the Regional Administrator for the parameters specified in 40 CFR Part 761, Polychlorinated Biphenyls. The manual provides a procedure for determining the contamination levels associated with a PCB spill as required under 761.10(e) and provides information on incinerator sampling methods and analytical procedures as required in the "Note" under 761.40.

1.2 Scope

Section 2 of this manual describes the sampling and analytical procedures for determining the contamination levels associated with a PCB spill.

Section 3 describes the procedures for measuring the flow rate of liquid and non-liquid PCBs fed to the combustion system. This task is required to be conducted in 40 CFR 761.40(a)(3) of the regulations.

The next section (Section 4) describes the procedures for monitoring incineration operations and combustion products. The continuous monitoring of combustion temperature during PCB incineration is required as specified in 40 CFR, 761.40(a)(4). Additionally, the continuous monitoring of CO and CO_2, and O_2 are required during the incineration of PCBs as prescribed under 40 CFR 761.40(a)(7).

Dwell time calculations and procedures for sampling and monitoring the scrubber water effluent are also included within Section 4.

Finally, the procedures for conducting and monitoring a trial or test burn are included in Section 5. When an incinerator is first used for the disposal of PCBs, or when modificatons are made that may affect the character of stack emission products, several parameters must be monitored, as specified under 40 CFR 761.40(a)(6). Additionally, trial burns may be required of the PCB disposal facility owner/operator by the Regional Administrator as discussed under 40 CFR 761.40(d)(2).

2.0 DETERMINATION OF PCB SPILL CONTAMINATION LEVEL

The following procedure describes where and how to sample in the event of a PCB spill in order to determine the extent of contamination.

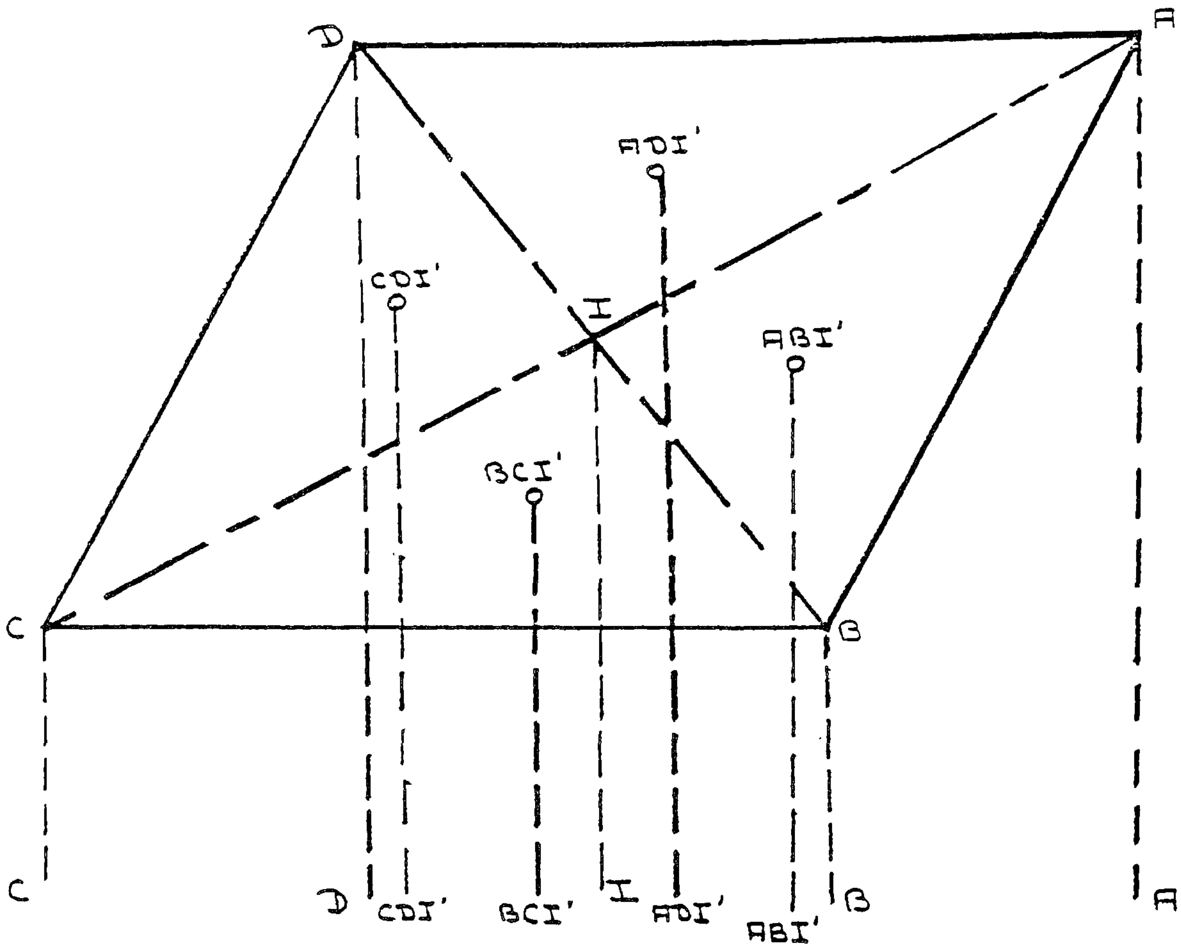
A three dimensional plot of the suspected zone of contamination should first be developed which defines the perimeter and depth of the suspected area.

The plot should be defined by establishing transects along the suspected perimeter with sufficient surface samples taken to define the perimeter. Transects for subsurface samples should also be established that intersect through the approximate center of the suspected area with subsurface samples taken at the perimeter intersection of the transects, the intersection of the transects at the approximate center of the suspected area, and at the approximate center of each segment formed by the perimeter and the transects. Figure 1 illustrates the designation of sample locations by use of transects.

Surface samples should be 500 gram samples taken at a depth of no greater than 2 millimeters. For suspected areas greater than 10 square meters, a surface sample point should consist of four surface samples taken at the corners of a one meter square grid with the four samples homogenized to make one composite sample.

Subsurface samples should be removed from the core at the elevation of interest, i.e., 0.3 meters deep, 0.6 meters deep, etc. The sample volume should be 100 gram samples taken at a depth of 0.3 meters or greater. The samples should then be prepared and analyzed for PCB content using the air-dried, 10 percent moisture added soxhlet extraction procedure (see Attachment A). If the analytical results at a 0.3 meter depth are below 500 parts per million PCBs, then it is presumed that the zone of contamination extends to 0.3 meters for purposes of practical excavation or removal. If the analytical results exceed 500 parts per million PCBs, then additional samples must be taken at successive 0.3 meter levels until the analytical results indicate a concentration below the 500 parts per million PCB level. Successive samples can be avoided by taking a sample at a depth assumed to be below the zone of contamination. If the concentration of PCBs is below 500 parts per million, then that sample

Figure 1: Designation of Sample Locations
By Use of Transects



KEY

Perimeter of Suspected Area- ABCD
Subsurface Samples
Perimeter Intersection of the Transects- AA, BB, CC, DD
Intersection of the Transects at the Approximate Center of the Suspected Area- II
Aproximate Center of Each Segment Formed by the Perimeter and the Transects- ABI'ABI', BCI'BCI', CDI'CDI', ADI'ADI'

point can be used to define the outer limit of the zone of contamination. When excavation activities are believed to be completed, samples should be taken at the excavated depth to determine if the excavation process has caused contamination at depths below the originally defined contaminated zone.[1]

3.0 PROCEDURES FOR MONITORING FEED RATE

3.1 Liquid PCB Wastes

The flow rate of liquids is normally determined by measuring the pressure drop across an orifice of known size. The pressure drop is converted to flow rate via fundamental engineering calculations. However, other devices are more commonly used to measure the liquid flow such as ones based on mechanically driven propellors or more advanced instruments based on magnetic measurements. Such devices are used widely and available commercially. Information on their installation, operation, etc., is supplied and should be obtained from the various vendors. No special consideration for PCB wastes are necessary compared to other liquids; consequently, detailed procedures are not specified in this manual.

However, it is recommended that instruments be selected which provide a continual real-time measurement of the flow rate in such a manner that the data can be visually displayed and automatically recorded. It should also be pointed out that the instruments discussed above, which measure the flow rate directly, indicate the bulk flow rate of the entire liquid. If the flow rate of PCBs is needed, it is necessary to determine the concentration of PCBs in the liquid waste feed. Sample preparation and analytical procedures for this purpose are identical to those specified for scrubber water in Section 4.3 of this manual. The bulk flow rate is simply multiplied by the percent of PCBs (by weight) in the feed to calculate the feed rate of PCBs.

3.2 Solid PCB Wastes

The flow rate of solids is normally determined by weighing loads and monitoring the time frequency at which these wastes are fed into the incinerator. Conveyor belts or other feed mechanisms can be equipped with scales for this purpose. As with liquid flow measurements, detailed procedures are not needed for such site specific techniques.

Load weights should be determined by weighing several representative loads and averaging them. Typically, in batch operations, the number of loads in a specific time, such as one hour, are merely counted by the operator. Sophisticated time frequency measurements are usually not practical during normal incineration operations. Flow rates should be calculated and recorded at least several times per day.

As with liquid wastes, if the feed rate of PCBs is needed, it is necessary to determine the concentration of PCBs in the feed material and multiply the % PCBs by the bulk feed rate.

4.0 PROCEDURES FOR MONITORING INCINERATION OPERATIONS AND COMBUSTION PRODUCTS

4.1 Temperature

Temperature should be routinely monitored and recorded at several locations within the combustion zone of the chemical waste incinerator, since it is an excellent indicator of the performance of the combustion process. The choice of temperature monitoring equipment and its placement or location within the combustion zone will vary depending on the particular design of the incinerator. Typically, flame temperature, afterburner temperature, hot duct temperature, and wall temperatures are monitored.

Combustion temperature is usually thought of as a value or range of values which typify the temperature at which chemical wastes introduced into the combustion chamber are subjected. Wastes introduced into the combustion zone are first heated rapidly to the appropriate flame temperature and then normally cool over time and distance from the flame. Temperatures within the combustion zones therefore can vary over a wide range.

In order to insure that PCB wastes are subjected to adequate temperature and dwell time conditions, the following specific minimum criteria have been specified in the regulation (40 CFR Part 761) as combustion criteria:

(1) Maintenance of the introduced PCB wastes for a 2-second dwell time at 1200°C (±100°C) and 3 percent excess oxygen in the stack gas, or

(2) Maintenance of the introduced PCB wastes for a 1½-second dwell time at 1600°C (± 100°C) and 2 percent excess oxygen in the stack gas.

4.1.1 Temperature Monitoring Locations

Compliance with the above criteria can be insured by maintaining a temperature above the required minimum temperature in the coldest portions of the combustion chamber. Accordingly, at least one temperature monitor should be located in this area, which typically is the furthest point from the flame, such as the point prior to the combustion zone exit. Specific locational requirements and the number and type of temperature monitors should be based upon consideration of particular designs. However, at least two monitors will normally be required, other than flame temperature monitors, in order to insure representative monitoring of the combustion chamber.

4.1.2 Temperature Monitoring Equipment Selection

Temperature monitoring within the combusiton zone should be performed with thermocouples which are selected for the appropriate characteristics, in accordance with the composition, size and construction factors. To assist in the selection of a proper thermocouple, summary tables and curves are provided in Tables 1 through 4 and Figures 2 and 3 (see Perry's Chemical Engineers Handbook, 4th Edition, for a more detailed discussion).

Radiation pyrometers should be used to monitor flame temperature if the flame is hotter than the practical operating range of thermocouples. Combustion temperature should also be monitored by thermocouples shielded from the flame in order to detect gas temperatures free of hot surface radiation effects. As specified in the regulation (40 CFR Part 761), the thermocouples should be accurate to within 100°C of the true temperature.

The thermocouple equipment choice must take into account maintenance requirements and operating limitations and should provide a continuous visual display of combustion temperature which automatically records the data.

Table 1: Common Types of Thermocouples and Temperature Ranges in Which They Are Used

I.S.A. type	Positive element	Negative element	Usual temp. range		Max. temp	
			°C.	°F.	°C.	°F.
S	90% Pt-10% Rh	Platinum	0 to 1450	32 to 2650	1700	3100
R	87% Pt-13% Rh	Platinum	0 to 1450	32 to 2650	1700	3100
K	Chromel-P	Alumel	−200 to 1100	−300 to 2000	1200	2200
J, Y	Iron	Constantan	−200 to 750	−300 to 1400	1000	1800
T	Copper	Constantan	−200 to 350	−200 to 650	600	1100
	Chromel-P	Constantan	−100 to 1000	−150 to 1800	1000	1800

(Perry's Chemical Engineers' Handbook, 4th Edition, p. 22-6)

Table 2: Corrosion Characteristics of Common Thermocouples

Type of Thermocouple	Influence of Temperature and Gas Atmospheres
Platinum vs. platinum-rhodium	1. Resistance to oxidizing atmosphere: very good 2. Resistance to reducing atmosphere: poor 3. Platinum corrodes easily above 1000°C. Should be used in gastight ceramic protecting tube
Chromel-P vs. Alumel	1. Resistance to oxidizing atmosphere: good to very good 2. Resistance to reducing atmosphere: poor 3. Affected by sulfur, reducing or sulfurous gas, SO_2, and H_2S
Iron vs. Constantan..........	1. Oxidizing and reducing atmospheres have little effect on accuracy. Best used in dry atmospheres 2. Resistance to oxidation: good up to 400°C. but poor above 700°C. 3. Resistance to reducing atmosphere: good (up to 400°C.) 4. Protect from oxygen, moisture, sulfur
Copper vs. Constantan....... ...	1. Subject to oxidation and alteration above 400°C. due to copper, above 600°C. due to Constantan wire. Contamination of copper affects calibration greatly 2. Resistance to oxidizing atmosphere: good 3. Resistance to reducing atmosphere: good 4. Requires protection from acid fumes
Chromel-P vs. Constantan...	1. Chromel attacked by sulfurous atmosphere 2. Resistance to oxidation: good 3. Resistance to reducing atmosphere: good

(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

Table 3: Methods of Joining Thermocouple Wires

Type of thermocouple	Method of joining	Flux
Platinum vs. platinum-rhodium....	Oxy-gas flame weld	None
	Electric-arc weld	None
Chromel-P vs. Alumel....	Oxyacetylene or oxy-gas flame weld	Borax, fluorite
	Electric-arc weld	None
	Silver solder	Borax
	Electric-resistance weld	None
Iron vs. Constantan	Oxyacetylene or oxy-gas flame weld	Borax, fluorite
	Electric-arc weld	None
	Silver solder	Borax
	Soft solder	Rosin
	Electric-resistance weld	None
Copper vs. Constantan .	Electric-arc weld	None
	Silver solder	Borax
	Soft solder	Rosin
Chromel-P vs. Constantan	Oxyacetylene or oxy-gas flame weld	Borax, fluorite
	Electric-arc weld	None
	Silver solder	Borax

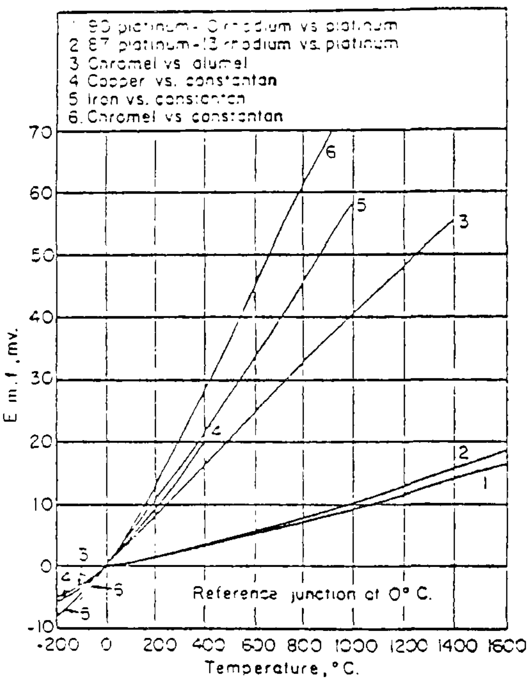
(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

Table 4: Recommended Maximum Operating Temperature of Thermocouple Protecting Tubes

Type of tube	Recommended max. temp. °C.	°F.
Metal Tubes		
High silicon iron..........	425	800
Seamless steel...	550	1000
Carbon steel...	550	1000
Cast iron......	700	1300
Wrought iron	700	1300
18 Cr-8 Ni stainless steel..	950	1800
28 Cr iron.......	1100	2000
Chromel T...	1100	2000
Nichrome.........	1100	2000
Nickel.........	1100	2000
20 Cr-32 Ni-48 Fe (Incoloy)..	1100	2000
Inconel..........	1260	2300
Ceramic Tubes		
Fused silica.......	1050	1900
Fire clay...........	1550	2800
Sillimanite....	1550	2800
Mullite......	1550	2800
Silica...............	1600	2900
Silicon carbide ..	1650	3000

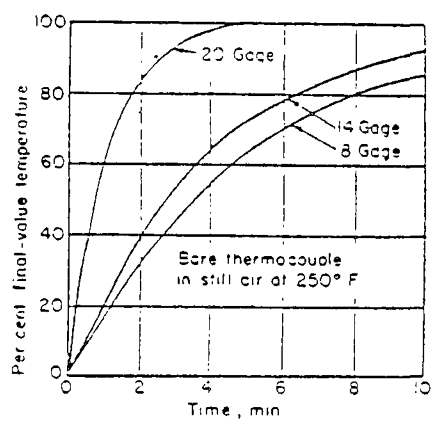
(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

Figure 2: Temperature-Thermal E.M.F Curves for Common Types of Thermocouples



(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

Figure 3: Response of Bare Thermocouples of Different Size



(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

4.2 Dwell Time

Dwell time or residence time is the amount of time in which a waste is subjected within the combustion zone to the combustion temperatures. This time should be estimated on the basis of flow rate calculations.

The least complex calculations for the average dwell time of combustion gases is equal to the volume of the combustion chamber divided by the volumetric flow rate of the gas corrected for temperature and pressure as shown below:

$$\text{DWELL TIME} = \frac{\text{Volume of combustion chamber}}{\text{Volumetric flow rate of gas thru chamber}}$$

where,

$$\text{Volumetric flow rate of gas} = \frac{\text{Mass flow rate of fuel + mass flow rate of air}}{\text{Density of Air @ T}} \times \frac{\text{Atmospheric Pressure}}{\text{Combustion Chamber Pressure}}$$

and,

T = Temperature of gases in combustion chamber

(Note: Mass flow rate of fuel includes any combustible gases derived from the waste.)

Example Calculation

If an incinerator includes a primary combustion chamber of 100 FT^3 and an after burn chamber of 2000 FT^3, fuel rate = 10,000#/hour, air rate = 90,000#/hour, primary chamber temperature - 3000°F, afterburner temperature = 2500°F, chamber pressure = 5 psig = 20 psia

Vol Furnace = 100 FT^3 + 2000 FT^3 = 2100 FT^3 at T = 2500°F

$$\text{Volumetric flow rate} = \frac{10{,}000\# + 90{,}000\# \times 15 \text{ psia}}{3600 \text{ SEC} \times .0134\#/\text{FT}^3 \times 20 \text{ psia}} = 1554 \text{ FT}^3/\text{sec}$$

then,

$$\text{Dwell Time} = \frac{2100}{1554} = 1.35 \text{ SEC}$$

(Note: The density of air at various temperatures may be calculated using the following formula.)

$$\text{Density} = \frac{\text{Ambient Temperature } (^{\circ}\text{K})}{13.1 \times \text{Combustion Temperature } (^{\circ}\text{K})}$$

or it may be obtained from prepared tables. Such tables can be found in the North American Combustion Handbook, North American Manufacturing, Inc.

The above calculation is a good technique for estimating residence time; however, the true residence time cannot be easily calculated on a theoretical basis since the effects of turbulence are difficult to model. The most accurate technique for determining dwell time is via actual test measurements. Such tests can be made by physically introducing a tracer gas such as radioactive argon into the incinerator and timing the tracer gas as it passes through the combustion chamber. The state-of-the-art and expensive equipment associated with such tests may make this technique impractical at most facilities.

4.3 Scrubber Water Monitoring

Scrubber effluent samples should be taken prior to, during, and after PCB incineration.

Samples of the quench/scrubber water can be taken from several points depending on the facility design. Listed in decreasing order of preference for obtaining a composite sample are: (1) a holding tank for ponds containing all the scrubber solution used during a burn, (2) a recirculation tank for scrubber solutions being recycled, and (3) a pipe through which these scrubber solutions are being pumped. The advantage of collecting a sample from holding tanks or ponds is that it is a composite sample and, as such, can be obtained without the requirement for collecting frequent grab samples or using automated sampling equipment.

Samples can be collected from valves on tanks or pipes containing the scrubber solution. If such valves are not available, a dip tube or sampling bottle device can be dropped into the tank or pond and allowed to fill. If grab samples are required to be taken, the facility owner/operator should mix all samples into a tank or drum. A composite sample should then be taken as described above. (All sample locations should be noted for consistency when future samples are taken.) The scrubber effluent samples should then be transferred to clean brown bottles equipped with polytetrafluoroethylene (PTFE) lined bottle caps and stored in a cool area.

To prepare the sample for analysis, 1.5 liter aliquots of the scrubber water samples should be extracted for organics using the separatory funnel extraction process for oil and grease from water. This procedure is described in the EPA Handbook on Methods for Chemical Analyses of Water and Wastes (EPA

626/6-74-003 MERC, Cincinnati, Ohio 45268). Pentane or methylene chloride can be substituted for Freon. The extracts should be dried by passing the sample through a 200 x 10.5 mm glass column containing a 50 mm bed of sodium sulfate which has been pre-extracted with pentane in a soxhlet for 24 hours. The extracts should then be concentrated to a 10 milliliter sample using a Kuderna - Danish concentrating evaporator. Characterization of the scrubber effluent samples should also be prepared.

The prepared sample is now ready to be analyzed for PCB content by gas chromatography-mass spectography. (See Attachment B.)

4.4 Continuous Stack Monitoring

The PCB marking and disposal regulation (40 CFR Part 761) requires continuous stack monitoring for CO, CO_2, and O_2. The purpose for these analyses is in part, to insure 99% combustion efficiency, specified as:

$$\frac{Cco_2}{Cco + Cco_2} \times 100$$

Where Cco and Cco_2 are the concentrations of carbon monoxide and carbon dioxide, respectively. Additionally, O_2 is analyzed to insure compliance with excess air requirements.

Carbon monoxide should be continuously measured in the stack of incinerators while burning PCBs as specified in CFR 60, Appendix A, Method 10 (Determination of carbon monoxide emissions from stationary sources). This method utilizes a nondispersive infrared (NDIR) analyzer, and is included in Attachment C of this manual.

Carbon dioxide in the stack should also be continuously monitored using a NDIR analyzer. The instrument should be accurate to ± 1 percent of full scale. A Cco_2 concentration of 0.05 - 5% and 0.02 - 20% is needed. Excess oxygen in the stack should be continuously monitored using paramagnetic or electrochemical instrumentation accurate to within ± 1% of full scale. A O_2 concentration range of 0.05 - 5%, 0.25 - 25% and 1 - 100% are needed.

5. PROCEDURE FOR CONDUCTING AND MONITORING A TEST BURN

5.1 Performance

The test burn should be conducted under conditions simulating normal operations. All effluent streams should be carefully monitored so that the environmental performance of the incinerator can be evaluated. The test should last approximately one day, consisting of the following 3 steps:

1) Start-up. The incinerator is fired with fuel only to purge the system and bring it up to steady-state at normal operating conditions.
2) Waste burn. The PCB waste is introduced into the incinerator at expected normal feed rates.

The test should only be as long as necessary to collect sufficient samples for analysis. A four hour run will probably suffice.

3) Shut-down. Waste feed is terminated and the incinerator is shut-down per normal procedures.

Prior to the test burn, PCB waste samples should be obtained and analyzed for their PCB concentrations, bulk waste feed rates should be determined, and feed rates of PCBs calculated.

The incinerator should be equipped with all necessary instruments and controls, as specified in 40 CFR Part 761. This should include provisions for continuous monitoring of combustion temperature, feed rates, and CO, CO_2 and O_2 in the stack. (See Section 4.0 of this manual for more details.) Additionally, stack sampling equipment for non-continuous monitoring for specified pollutant concentrations should be installed and prepared as specified in section 5.2 of this manual. All instruments should be calibrated.

Prior to start-up, all ash should be removed from the incinerator and the scrubber system should be purged and filled with a fresh solution.

As soon as steady-state conditions are reached during the start-up phase of the test, conditions should be noted and samples collected to characterize background conditions.

When the monitoring equipment is ready for collecting the next set of samples, the PCB waste should be introduced into the incinerator. During the test, samples should be collected and records kept of the readings of the continuous monitors. Visual observation of the plume should also be made.

The following safety procedures should be established and followed:

- Only authorized personnel should be permitted in the test area during operations.
- Waste handling must be performed only by personnel wearing suitable protective clothing and trained in handling such materials.
- Visual observation of the test system must be maintained at all times during operation.
- Canister gas masks and emergency oxygen resuscitation units must be available in the immediate test burn area.

5.2 COMBUSTION PRODUCTS

Non-continuous stack monitoring for CO, CO_2, O_2, HCl, total particulate matter, NO_x, total chlorinated organic content (RCL) and PCB chemical substances, should be conducted as specified below.

5.2.1 <u>CO, CO_2, O_2</u>

Stack concentrations of carbon monoxide, carbon dioxide and oxygen should be determined as specified in 40 CFR 60, EPA Method number 3, which is provided in Attachment D of this manual.

5.2.2 <u>HCl</u>

Stack concentration for hydrogen chloride should be determined by collecting the hydrogen chloride in an impinger filled with a caustic solution, such as dilute sodium hydroxide or sodium bicarbonate.

This solution should then be analyzed for chloride ion concentrations using the mercuric nitrate method. This method is described in <u>Methods of Air Sampling and Analysis</u>, 2nd Edition, and in <u>Standard Methods for the Examination of Water and Wastewater</u>. Both are publications of the American Public Health Association.

5.2.3 <u>RCL and PCBs</u>

Samples for analysis of total chlorinated organic content (which includes PCBs) should be collected on a solid sorbent trap, such as XAD-2 Amberlite Resin. Temperature control must be maintained since the absorptive characteristics of the trap change with temperature differences. The solid sorbent trap should be located in the sampling train downstream from the heated filter and upstream of the first impinger.

The sample is then removed from the solid sorbent trap via a 24 hour soxhlet extraction with both pentanol and methanol. The extracts should be dried with sodium sulfate and concentrated to 10 ml. (A more detailed description of this sampling method is provided in Attachment E.)

Finally, the sample is analyzed for PCB and RCL content by Gas Chromotography-Mass Spectography (see Attachment B).

5.2.4 NO_x

Stack concentrations of nitrogen oxide(s) should be determined as specified in 40 CFR 60, EPA Method number 7, which is provided in Attachment F of this manual.

5.2.5 Total Particulate Matter

Mass emission rates of total particulate matter should be determined as specified in 40 CFR 60, Method 5, which is provided in Attachment G of this manual.

REFERENCES

1. Determination of PCB Spill Contamination Levels, Unpublished report. Available from Hal Snyder, EPA/Office of Enforcement.

2. EPA Handbook on Methods for Chemical Analyses of Water and Wastes, EPA publication No. 629/6-74-003, MERC, Cincinnati, Ohio, 1974.

3. Standard Methods of Air Sampling and Analysis, 2nd edition, APHA, Washington, D.C., 1975.

4. Standard Methods for the Examination of Water and Wastewater, APHA, Washington, D.C., 1977.

5. Personal communication. Robert B. Burns, President, Industrial Hydronics Corporation, Princeton, N.J., to J. Howard Beard, III, Office of Solid Waste, U.S. EPA, January 1978.

6. Personal communication. James Stevens and Joan Berkowitz, Arthur D. Little, Inc., Cambridge, Massachusetts, to J. Howard Beard, III, Office of Solid Waste, U.S. EPA, January, 1978.

7. Personal communication. Carol A. Zee, TRW, Inc., Redondo Beach, California, to J. Howard Beard, III, Office of Solid Waste, U.S. EPA, January, 1978.

8. Analysis of Pesticide Residues in Human and Environmental Samples, EPA unpublished manuscript prepared by Pesticides and Toxic Substances Effects Laboratory, National Environmental Research Center, U.S. EPA, Research Triangle Park, N.C., 1974.

9. Personal communication. Christopher C. Shih, TRW, Redondo Beach, California, to J. Howard Beard, III, Office of Solid Waste, U.S. EPA, January 1978.

10. Destroying Chemical Wastes in Commercial Scale Incinerators, EPA Contract No. 68-01-2966, Facility Report #6, Office of Solid Waste, U.S. EPA, Washington, D.C., 1977.

11. Disposal of Organochloride Wastes by Incineration at Sea (EPA - 430/9-75-014), Washington, D.C., July 1975.

Attachment A

Tentative Method of Testing for
Polychlorinated Biphenyls in Spilled Material

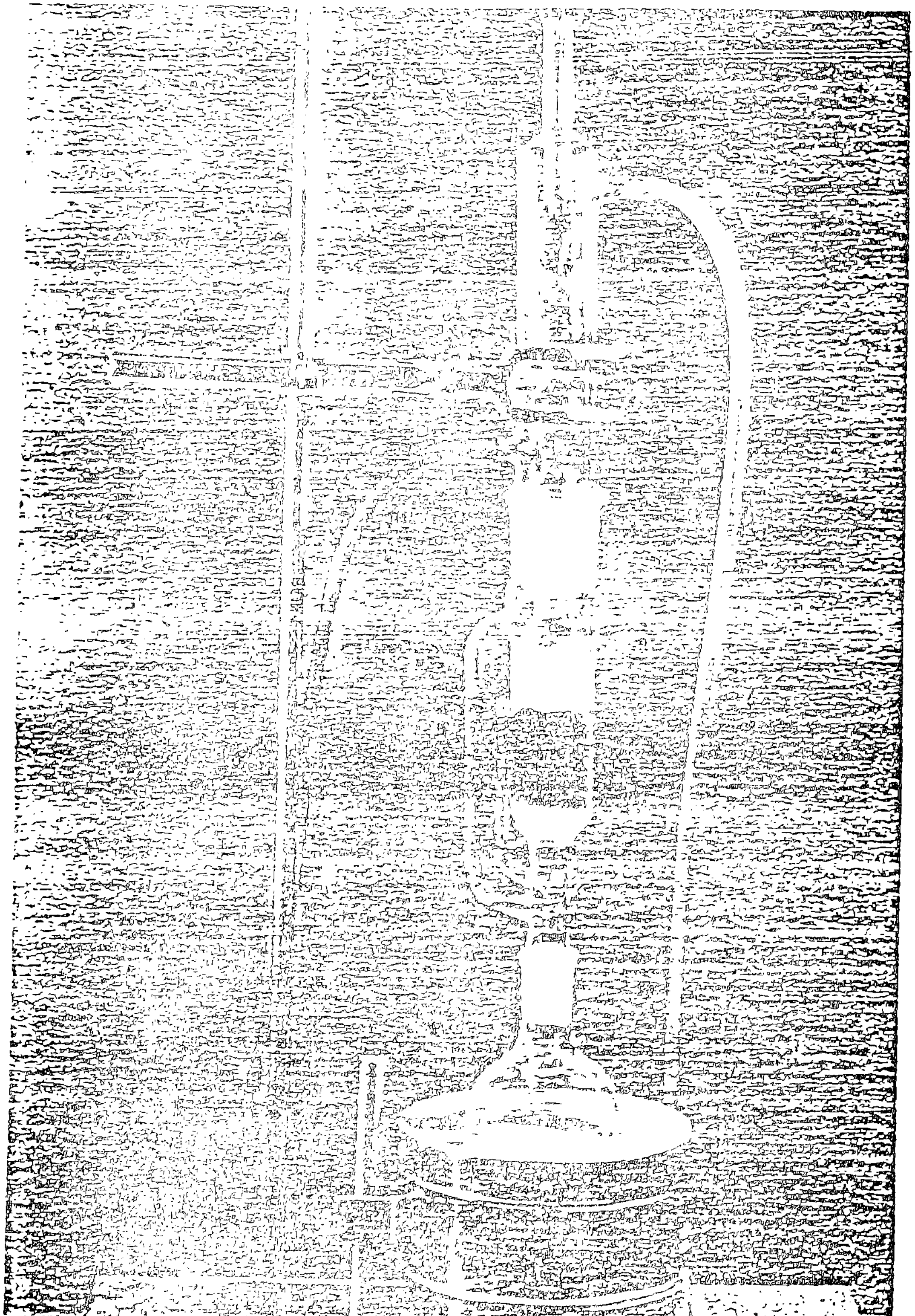
Tentative Method of Testing for Polychlorinated Biphenyls (PCBs) in Spilled Material

Any excess liquid is decanted and the sample is spread in a pyrex dish (8" wide x 12" long x 2" deep). The sample is air dried at room temperature for about 4 to 5 days in a contaminate free area. The dried sample is then ground with a procelain mortar and pestle to a uniform particle size.

The sample is then divided by mixing and quartering until a sub-sample of about 100 grams is obtained (for surface samples only). The sample is weighed in a 100-ml beaker. (Add 10 — 20 % water, seal and thoroughly mix by tumbling, and equilibrate (minimum 2 hours) prior to extraction.)

The extraction is then carried out in a soxhlet extractor (see Figure). Glass wool (about 1 inch deep) is packed in the bottom of the extraction chamber (40 x 150 mm). The weighed sample is added and an additional wad of glass wool is placed on the top. The sample is then extracted using 200 ml of hexane-acetone (9:1) for about 8 hours. The extraction may be carried out overnight or longer as may be necessary for heavily contaminated samples.

The extract (approximately 200 ml) is then transferred to a Kuderna-Danish (K-D) evaporator and concentrated to 6 - 10 ml on a warm water bath at approximately 70°C. (The remainder of the procedure is described in Method 3 (Method for Polychlorinated Biphenyls (PCBs) in Industrial Effluents) beginning with Section 9.4.)



Soxhlet Extraction of Bottom Samples

9.4 Qualitatively analyze the sample by gas chromatography with an electron capture detector. From the response obtained decide:

a. If there are any organochlorine pesticides present,

b. If there are any PCB's present,

c. If there is a combination of a and b,

d. If elemental sulfur is present,

e. If the response is too complex to determine a, b, or c.

f. If no response, concentrate to 1.0 ml or less, as required, according to EPA Method (4), pg. 28 and repeat the analysis looking for a, b, c, d, and e. Samples containing Aroclors with a low percentage of chlorine, eg. 1221 and 1232, may require this concentration in order to achieve the detection limit of 1 μg/l. Trace quantities of PCB's are often masked by background which usually occur in the samples.

9.5 If condition a exists, quantitatively determine the organochlorine pesticides according to (1).

9.6 If condition b exists, PCB's only are present, no further separation or cleanup is necessary. Quantitatively determine the PCB's according to 11. below.

9.7 If condition c exists, compare peaks obtained from the sample to those of standard Aroclors and make a judgment as to which Aroclors may be present. To separate the PCB's from the organochlorine pesticides, continue as outlined in 10.4.

9.8 If condition d exists separate the sulfur from the sample using the method outlined in (10.3) followed by the method in (10.5)

9.9 If condition e exists then the following macro cleanup and separation procedures (10.2 and 10.3) should be employed and, if necessary, followed by the micro separation procedures (10.4 and 10.5).

10. Cleanup and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as, the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether cleanup is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to remove fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for the compounds of interest.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-35 seconds. Extract with two 100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500 ml K-D flask equipped with a 10 ml ampul. Rinse the separatory funnel and column with three 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2. Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix I) in a Chromaflex column. After settling the Florisil by tapping the column add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500 ml K-D flasks equipped with 10 ml ampuls. (See Eluate Composition below). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate

Aldrin	DDT	Pentachloro-nitrobenzene
BHC	Heptachlor	Strobane
Chlordane	Heptachlor Epoxide	Toxaphene
DDD	Lindane	Trifluralin
DDE	Methoxychlor	PCB's
	Mirex	

15% Eluate	50% Eluate
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	
Phthalate esters	

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (6).

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Silica Gel Micro-Column Separation Procedure (7)

10.4.1 Activation for Silica Gel

10.4.1.1 Place about 20 gm of silica gel in a 100 ml beaker. Activate at 180 C for approximately 16 hours. Transfer the silica gel to a 100 ml glass stoppered bottle. When cool, cover with about 35 ml of 0.50% diethyl ether in benzene (volume:volume). Keep bottle well sealed. If silica gel collects on the ground glass surfaces, wash off with the above solvent before resealing. Always maintain an excess of the mixed solvent in bottle (approximately 1/2 in. above silica gel). Silica gel can be effectively stored in this manner for several days.

10.4.2 Preparation of the Chromatographic Column

10.4.2.1 Pack the lower 2 mm ID Section of the microcolumn with glass wool. Permanently mark the column 120 mm above the glass wool. Using a clean rubber bulb from a disposable pipet seal the lower end of the microcolumn. Fill the microcolumn with 0.50% ether in benzene (v:v) to the bottom of the 10/30 joint (Figure 1). Using a disposable capillary pipet, transfer several aliquots of the silica gel slurry into the microcolumn. After approximately 1 cm of silica gel collects in the bottom of the microcolumn, remove the rubber bulb seal, tap the column to insure that the silica gel settles uniformly. Carefully pack column until the silica gel reaches the 120 ± 2 mm mark. Be sure that there are no air bubbles in the column. Add about 10 mm of sodium sulfate to the top of the silica gel. Under low humidity conditions, the silica gel may coat the sides of the column and not settle properly. This can be minimized by wiping the outside of the column with an anti-static solution.

10.4.2.2 Deactivation of the Silica Gel

a. Fill the microcolumn to the base of the 10/30 joint with the 0.50% ether-benzene mixture, assemble reservoir (using spring clamps) and fill with approximately 15 ml of the 0.50% ether-benzene mixture. Attach the air pressure device (using spring clamps) and adjust the elution rate to approximately 1 ml/min. with the air pressure control. Release the air pressure and detach reservoir just as the last of the solvent enters the sodium sulfate. Fill the column with n-hexane (not mixed hexanes) to the base of the 10/30 fitting. Evaporate all residual benzene from the reservoir, assemble the reservoir section and fill with 5 ml of n-hexane. Apply air pressure and adjust the flow to 1 ml/min. (The n-hexane flows slightly faster than the benzene). Release the air pressure and remove the reservoir just as the n-hexane enters the sodium sulfate. The column is now ready for use.

b. Pipet a 1.0 ml aliquot of the concentrated sample extract (previously reduced to a total volume of 2.0 ml) on to the column.

As the last of the sample passes into the sodium sulfate layer, rinse down the internal wall of the column twice with 0.25 ml of n-hexane. Then assemble the upper section of the column. As the last of the n-hexane rinse reaches the surface of the sodium sulfate, add enough n-hexane (volume predetermined, see 10.4.3 below) to just elute all of the PCB's present in the sample. Apply air pressure and adjust until the flow is 1 ml/min. Collect the desired volume of eluate (predetermined, see 10.4.3 below) in an accurately calibrated ampul. As the last of the n-hexane reaches the surface of the sodium sulfate, release the air pressure and change the collection ampul.

c. Fill the column with 0.50% diethyl ether in benzene, again apply air pressure and adjust flow to 1 ml/min. Collect the eluate until all of the organochlorine pesticides of interest have been eluted (volume predetermined, see 10.4.3 below).

d. Analyze the eluates by gas chromatography.

10.4.3 Determination of Elution Volumes

10.4.3.1 The elution volumes for the PCB's and the pesticides depend upon a number of factors which are difficult to control. These include variation in:

a. Mesh size of the silica gel

b. Adsorption properties of the silica gel

c. Polar contaminants present in the eluting solvent

d. Polar materials present in the sample and sample solvent

e. The dimensions of the microcolumns

Therefore, the optimum elution volume must be experimentally determined each time a factor is changed. To determine the elution volumes, add standard mixtures of Aroclors and pesticides to the column and serially collect 1 ml elution volumes. Analyze the individual eluates by gas chromatography and determine the cut-off volume for n-hexane and for ether-benzene. Figure 2 shows the retention order of the various PCB components and of the pesticides. Using this information, prepare the mixtures required for calibration of the microcolumn.

10.4.3.2 In determining the volume of hexane required to elute the PCB's the sample volume (1 ml) and the volume of n-hexane used to rinse the column wall must be considered. Thus, if it is determined that a 10.0 ml elution volume is required to elute the PCB's, the volume of hexane to be added in addition to the sample volume but including the rinse volume should be 9.5 ml.

10.4.3.3 Figure 2 shows that as the average chlorine content of a PCB mixture decreases the solvent volume for complete elution increases. Qualitative determination (9.4) indicates which Aroclors are present and provides the basis for selection of the ideal elution volume. This helps to minimize the quantity of organochlorine pesticides which will elute along with the low percent chlorine PCB's and insures the most efficient separations possible for accurate analysis.

10.4.3.4 For critical analysis where the PCB's and pesticides are not separated completely, the column should be accurately calibrated according to (10.4.3.1) to determine the percent of material of interest that elutes in each fraction. Then flush the column with an additional 15 ml of 0.50% ether in benzene followed by 5 ml of n-hexane and use this reconditioned column for the sample separation. Using this technique one can accurately predict the amount (%) of materials in each micro column fraction.

10.5 Micro Column Separation of Sulfur, PCB's, and Pesticides

10.5.1 See procedure for preparation and packing micro column in PCB analysis section (10.4.1 and 10.4.2).

10.5.2 Microcolumn Calibration

10.5.2.1 Calibrate the microcolumn for sulfur and PCB separation by collecting 1.0 ml fractions and analyzing them by gas chromatography to determine the following:

1) The fraction with the first eluting PCB's (those present in 1260),
2) The fraction with the last eluting PCB's (those present in 1221),
3) The elution volume for sulfur,
4) The elution volume for the pesticides of interest in the 0.50% ether-benzene fraction

From these data determine the following:

1) The eluting volume containing only sulfur (Fraction I),
2) The eluting volume containing the last of the sulfur and the early eluting PCB's (Fraction II),
3) The eluting volume containing the remaining PCB's (Fraction III),
4) The ether-benzene eluting volume containing the pesticides of interest (Fraction IV).

10.5.3 Separation Procedure

10.5.3.1 Carefully concentrate the 6% eluate from the florisil column to 2.0 ml in the graduated ampul on a warm water bath.

10.5.3.2 Place 1.0 ml (50%) of the concentrate into the microcolumn with a 1 ml pipet. Be careful not to get any sulfur crystals into the pipet.

10.5.3.3 Collect Fractions I and II in calibrated centrifuge tubes.

Collect Fractions III and IV in calibrated ground glass stoppered ampules.

10.5.3.4 Sulfur Removal (9) - Add 1 to 2 drops of mercury to Fraction II stopper and place on a wrist-action shaker. A black precipitate indicates the presence of sulfur. After approxiately 20 minutes the mercury may become entirely reacted or deactivated by the precipitate. The sample should be quantitatively transferred to a clean centrifuge tube and additional mercury added. When crystals are present in the sample, three treatments may be necessary to remove all the sulfur. After all the sulfur has been removed from Fraction II (check using gas chromatography) combine Fractions II and III. Adjust the volume to 10 ml and analyze gas chromatography. Be sure no mercury is transferred to the combined Fractions II and III, since it can react with certain pesticides.

By combining Fractions II and III, if PCB's are present, it is possible to identify the Aroclor(s) present and a quantitative analysis can be performed accordingly. Fraction I can be discarded since it only contains the bulk of the sulfur. Analyze Fractions III and IV for the PCB's and pesticides. If DDT and its homologs, aldrin, heptachlor, or technical chlordane are present along with the PCB's, an additional micro-column separation can be performed which may help to further separate the PCB's from the pesticides (See 10.4).

11. Quantitative Determination

11.1 Measure the volume of n-hexane eluate, containing the PCB's and inject 1 to 5 µl into the gas chromatograph. If necessary, adjust the volume of the eluate to give linear response to the electron capture detector. The microcoulometric or the electrolytic detector may be employed to improve specificity for samples having higher concentrations of PCB's.

11.2 Calculations

11.2.1 When a single Aroclor is present, compare quantitative Aroclor reference standards (e.g., 1242, 1260) to the unknown. Measure and sum the areas of the unknown and the reference Aroclor and calculate the result as follows:

$$\text{Microgram/liter} = \frac{[A]\ [B]\ [V_t]}{[(V_i)\ (V_s)]} \times [N]$$

$$A = \frac{\text{ng of Standard Injected}}{\Sigma \text{ of Standard Peak Areas}} = \frac{ng}{mm^2}$$

B = Σ of Sample Peak Areas = (mm^2)

V_i = Volume of sample injected (µl)

V_t = Volume of Extract (µl) from which sample is injected into gas chromatograph

V_s = Volume of water sample extracted (ml)

N = 2 when micro column used
1 when micro column not used

Peak Area = Peak height (mm x Peak Width at 1/2 height

11.2.2 For complex situations, use the calibration method described below. Small variations in components between different Aroclor batches make it necessary to obtain samples of several specific Aroclors. These reference Aroclors can be obtained from Dr. Ronald Webb, Southest Environmental Research Laboratory, EPA, Athens, Georgia 30601. The procedure is as follows:

11.2.2.1 Using the OV-1 column, chromatograph a known quantity of each Aroclor reference standard. Also chromatograph a sample of p,p'-DDE. Suggested concentration of each standard is 0.1 ng/μl for the Aroclors and 0.02 ng/μl for the p,p'-DDE.

11.2.2.2 Determine the relative retention time (RRT) of each PCB peak in the resulting chromatograms using p,p'-DDE as 100. See Figures 3 through 5.

$$RRT = \frac{RT \times 100}{RT_{DDE}}$$

RRT = Relative Retention Time

RT = Retention time of peak of interest

RT_{DDE} = Retention time of p,p'-DDE

Retention time is measured as that distance in mm between the first appearance of the solvent peak and the maximum for the compound.

11.2.2.3 To calibrate the instrument for each PCB measure the area of each peak.

Area = Peak height (mm) x Peak width at 1/2 height. Using Tables 1 through 6 obtain the proper mean weight factor, then determine the response factor ng/mm^2.

$$ng/mm^2 = \frac{(ng_i)\ \frac{(\text{mean weight percent})}{100}}{(\text{Area})}$$

ng_i = ng of Aroclor Standard Injected

Mean weight percent = obtained from Tables 1 through 6.

11.2.2.4 Calculate the RRT value and the area for each PCB peak in the sample chromatogram. Compare the sample chromatogram to those obtained for each reference Aroclor standard. If it is apparent that the PCB peaks present are due to only one Aroclor then calculate the concentration of each PCB using the following formula:

ng PCB = ng/mm^2 x Area

Where Area = Area (mm^2) of sample peak

ng/mm^2 = Response factor for that peak measured.

Then add the nanograms of PCB's present in the injection to get the total number of nanograms of PCB's present. Use the following formula to calculate the concentration of PCB's in the sample

$$\text{Micrograms/Liter} = \frac{[ng]\ \ [V_t]}{[V_s]\ \ [V_i]} \times [N]$$

V_s = volume of water extracted (ml)

V_t = volume of extract (µl)

V_i = volume of sample injected (µl)

Σng = sum of all the PCB's in nanograms for that Aroclor identified

N = 2 when microcolumn used

N = 1 when microcolumn not used

The value can then be reported as Micrograms/ Liter PCB's reported as the Aroclor For samples containing more than one Aroclor, use Figure 9 chromatogram divisional flow chart to assign a proper response factor to each peak and also identify the "most likely" Aroclors present. Calculate the ng of each PCB isomer present and sum them according to the divisional flow chart. Using the formula above, calculate the concentration of the various Aroclors present in the sample.

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

Table 1

Composition of Aroclor 1221 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	31.8	15.8	1
14	19.3	9.1	1
16	10.1	9.7	2
19	2.8	9.7	2
21	20.8	9.3	2
28	5.4	13.9	[2 85% 3] 15%
32	1.4	30.1	[2 10% 3] 90%
[37 40]	1.7	48.8	3 3
Total	93.3		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of seventeen results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 2

Composition of Aroclor 1232 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	16.2	3.4	1
14	9.9	2.5	1
16	7.1	6.8	2
[20 21]	17.8	2.4	2 2
28	9.6	3.4	2] 40% 3] 60%
32	3.9	4.7	3
37	6.8	2.5	3
40	6.4	2.7	3
47	4.2	4.1	4
54	3.4	3.4	3] 33% 4] 67%
58	2.6	3.7	4
70	4.6	3.1	4] 90% 5] 10%
78	1.7	7.5	4
Total	94.2		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of four results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 3

Composition of Aroclor 1242 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2] 25% 3] 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3] 33% 4] 67%
58	5.6	3.3	4
70	10.3	2.8	4] 90% 5] 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	2.3	16.4	5
125	1.6	20.4	5] 85% 6] 15%
146	1.0	19.9	5] 75% 6] 25%
Total	98.5		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 4

Composition of Aroclor 1248 (S)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
21	1.2	23.9	2
28	5.2	3.3	3
32	3.2	3.8	3
47	8.3	3.6	3
40	8.3	3.9	3] 85% 4] 15%
47	15.6	1.1	4
54	9.7	6.0	3] 10% 4] 90%
58	9.3	5.8	4
70	19.0	1.4	4] 80% 5] 20%
78	6.6	2.7	4
84	4.9	2.6	5
98	3.2	3.2	5
104	3.3	3.6	4] 10% 5] 90%
112	1.2	6.6	5
125	2.6	5.9	5] 90% 6] 10%
146	1.5	10.0	5] 85% 6] 15%
Total	103.1		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 5

Composition of Aroclor 1254 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4] 25% 5] 75%
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5] 70% 6] 30%
146	10.4	2.7	5] 30% 6] 70%
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers are bracketed.

Table 6

Composition of Aroclor 1260 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
[98	3.8	3.5	[d]
104]			5 60%
			6 40%
117	3.3	6.7	6
125	12.3	3.3	5 15%
			6 85%
146	14.1	3.6	6
160	4.9	2.2	6 50%
			7 50%
174	12.4	2.7	6
203	9.3	4.0	6 10%
			7 90%
[232			[e]
244]	9.8	3.4	6 10%
			7 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

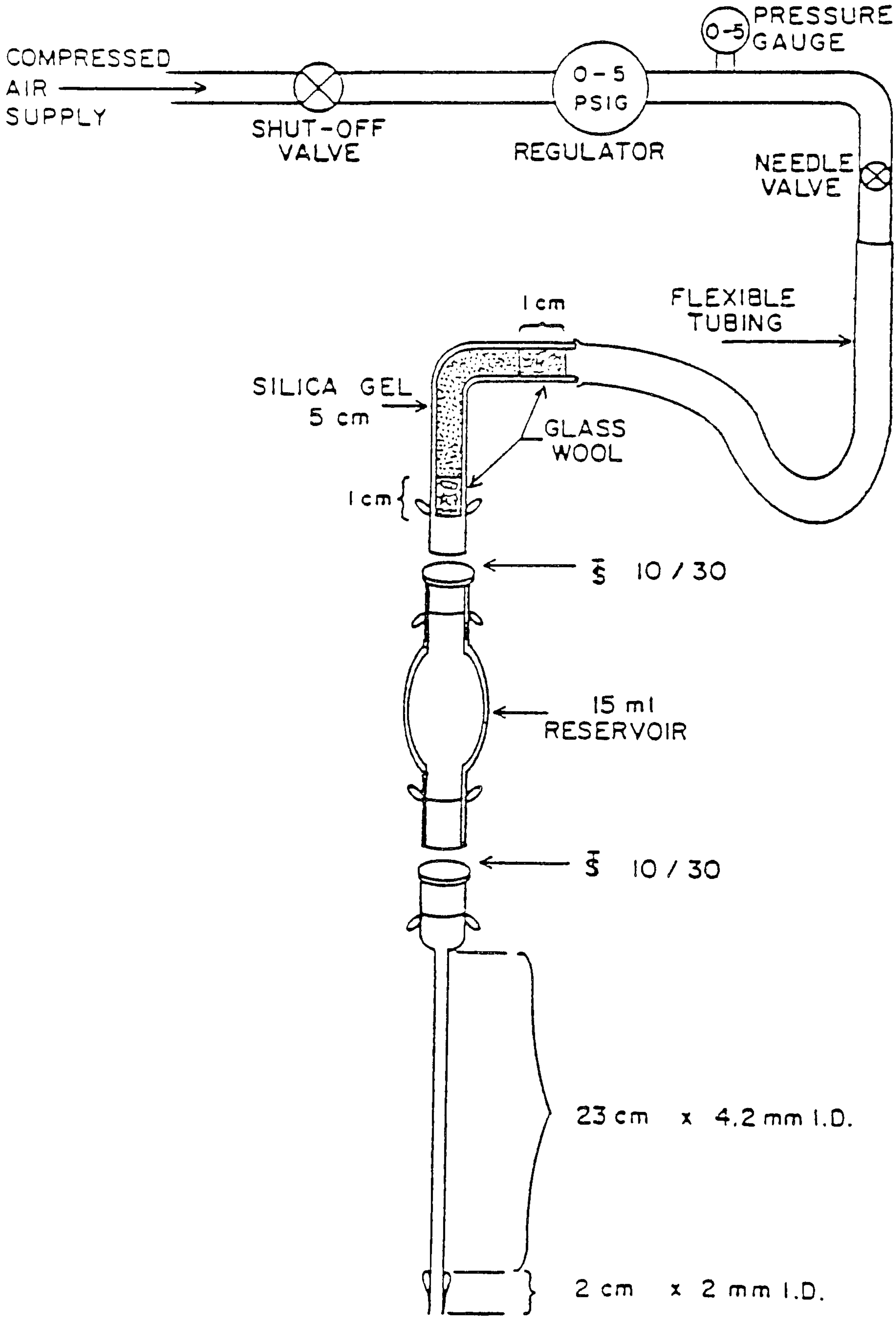
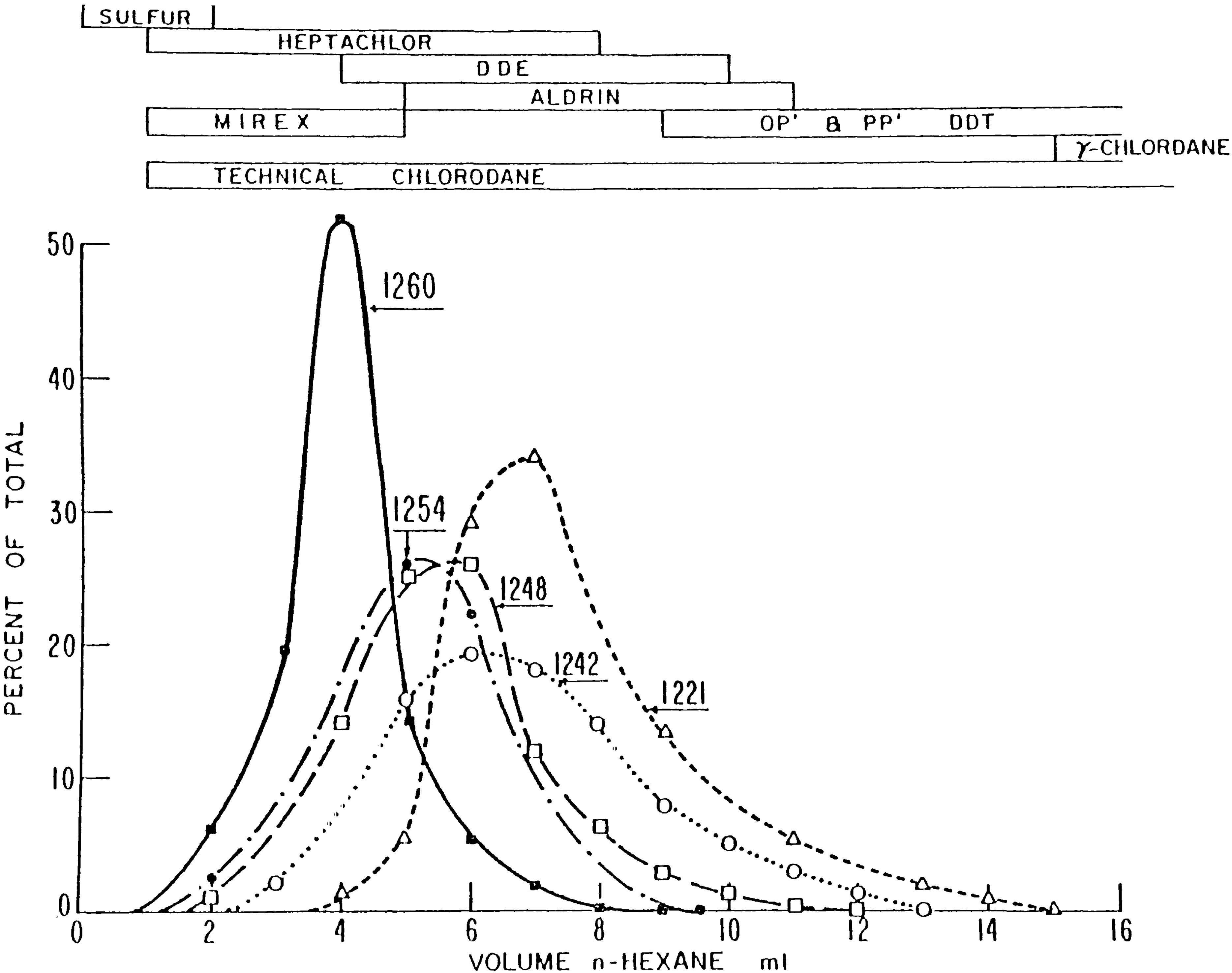


FIGURE 1. MICROCOLUMN SYSTEM



SULFUR
HEPTACHLOR
DDE
ALDRIN
MIREX
OP' & PP' DDT
γ-CHLORDANE
TECHNICAL CHLORODANE
1260
1254
1248
1242
1221
PERCENT OF TOTAL
VOLUME n-HEXANE ml
0
2
4
6
8
10
12
14
16
10
20
30
40
50

REFERENCES

(1) "Method for Organochlorine Pesticides in Industrial Effluents," U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1973.

(2) Leoni, V., "The Separation of Fifty Pesticides and Related Compounds and Polychlorinated Biphenyls into Four Groups by Silica Gel Micro-column Chromatography," Journal of Chromatography, 62, 63 (1971).

(3) McClure, V. E., "Precisely Deactivated Adsorbents Applied to the Separation of Chlorinated Hydrocarbons," Journal of Chromatography, 70, 168 (1972).

(4) "Methods for Organic Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1971.

(5) "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," Chapter 6, Section 6.4, U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1972.

(6) "Pesticide Analytical Manual," U.S. Dept. of Health, Education, and Welfare, Food and Drug Administration, Washington, D.C.

(7) Bellar, T. A. and Lichtenberg, J. J., "Method for the Determination of Polychlorinated Biphenyls in Water and Sediment," U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1973.

(8) Webb, R. G. and McCall, A. C., "Quantitative PCB Standards for Electron Capture Gas Chromatography." Presented at the 164th National ACS Meeting, New York, August 29, 1972. (Submitted to the Journal of Chromatographic Science for publication).

(9) Goerlitz, D. F. and Law, L. M., "Note on Removal of Sulfur Interferences from Sediment Extracts for Pesticide Analysis," Bulletin of Environmental Contamination and Toxicology, 6, 9 (1971).

(10) Mills, P. A., "Variation of Florisil Activity: Sample Method for Measuring Adsorbent Capacity and its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29 (1968).

(11) Steere, N. V., editor, "Handbook of Laboratory Safety," Chemical Rubber Company, 18901 Cranwood Parkway, Cleveland, Ohio 44128, 1971, pp. 250-254.

APPENDIX I

13. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6) (S). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus

13.2.1 Buret. -- 25 ml with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks. -- 125 ml narrow mouth and 25 ml, glass stoppered.

13.2.3 Pipet. -- 10 and 20 ml transfer.

13.2.4 Volumetric flasks. -- 500 ml.

13.3 Reagents and Solvents

13.3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane. -- Distilled from all glass apparatus.

13.3.3 Lauric acid. --Purified, CP.

13.3.4 Lauric acid solution. -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

13.3.5 Phenolphthalein Indicator. -- Dissolve 1 g in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. -- Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure

13.4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernatant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05N to a permanent end point.

13.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

13.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 13.6.

13.6 Test for Proper Elution Pattern and Recovery of Pesticides: Prepare a test mixture containing aldrin, heptachlor epoxide p,p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate and the others in the 6% eluate.

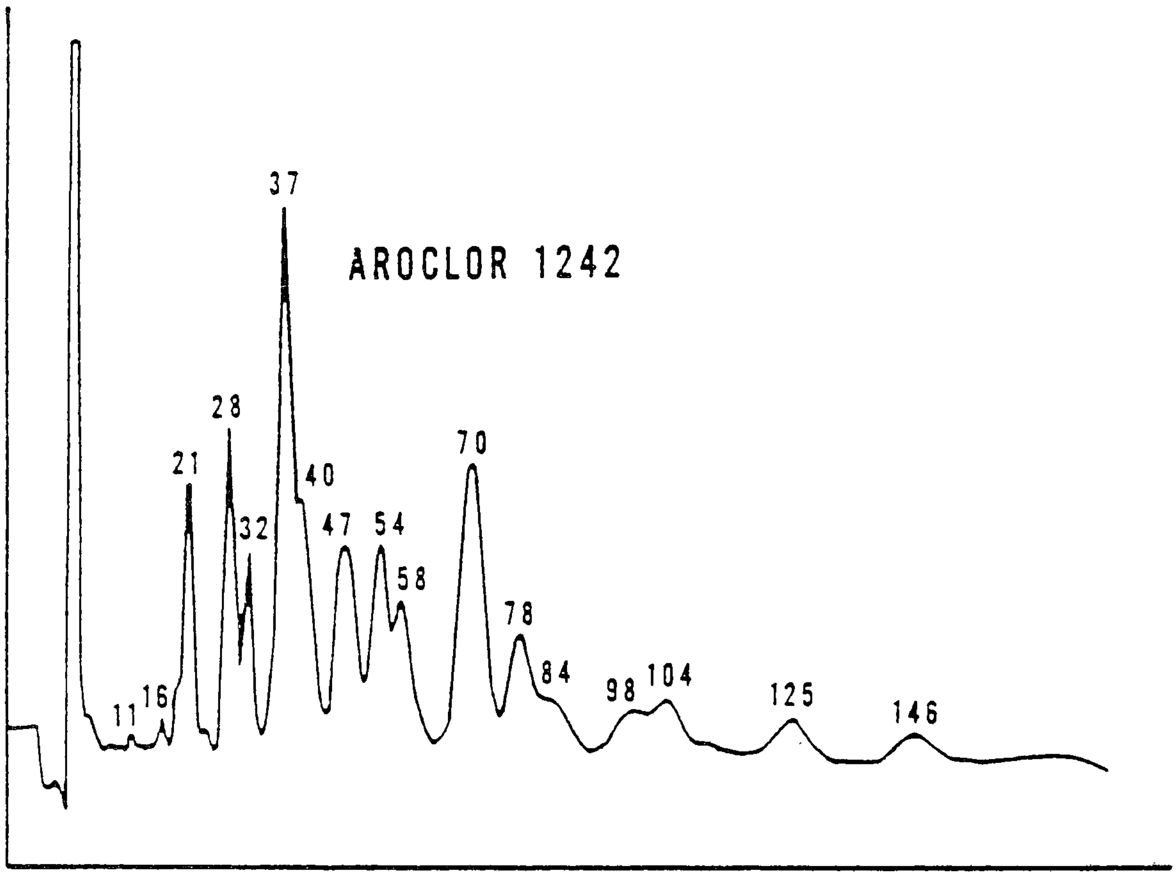


Figure 3. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min,
Column Temperature: 170 C, Detector: Electron Capture

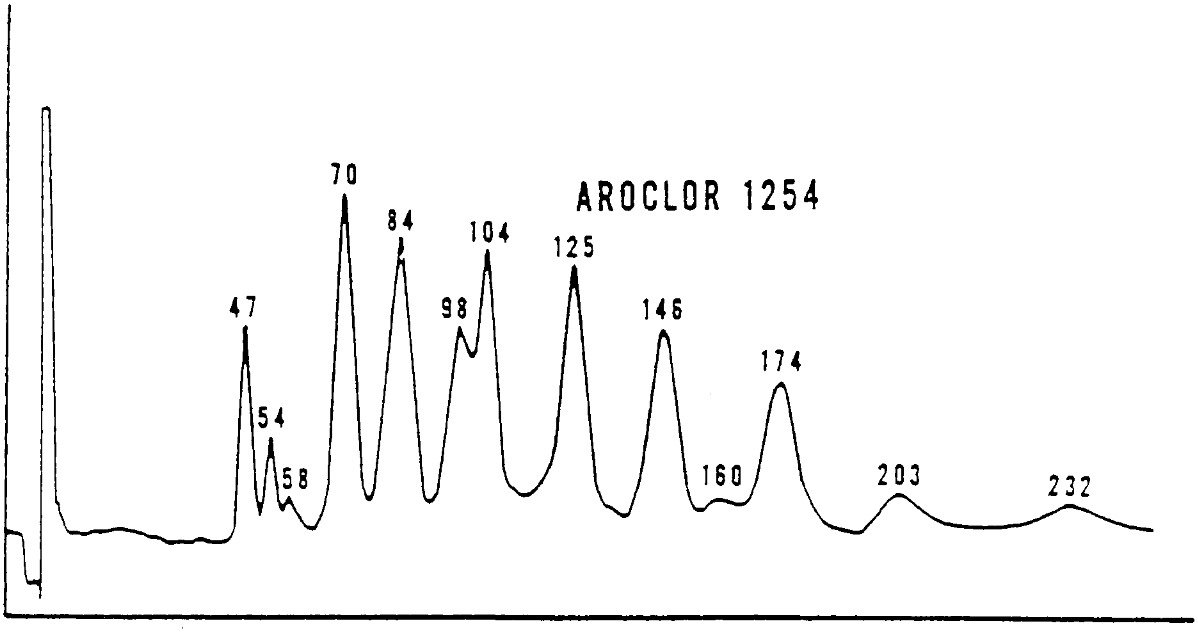


Figure 4. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

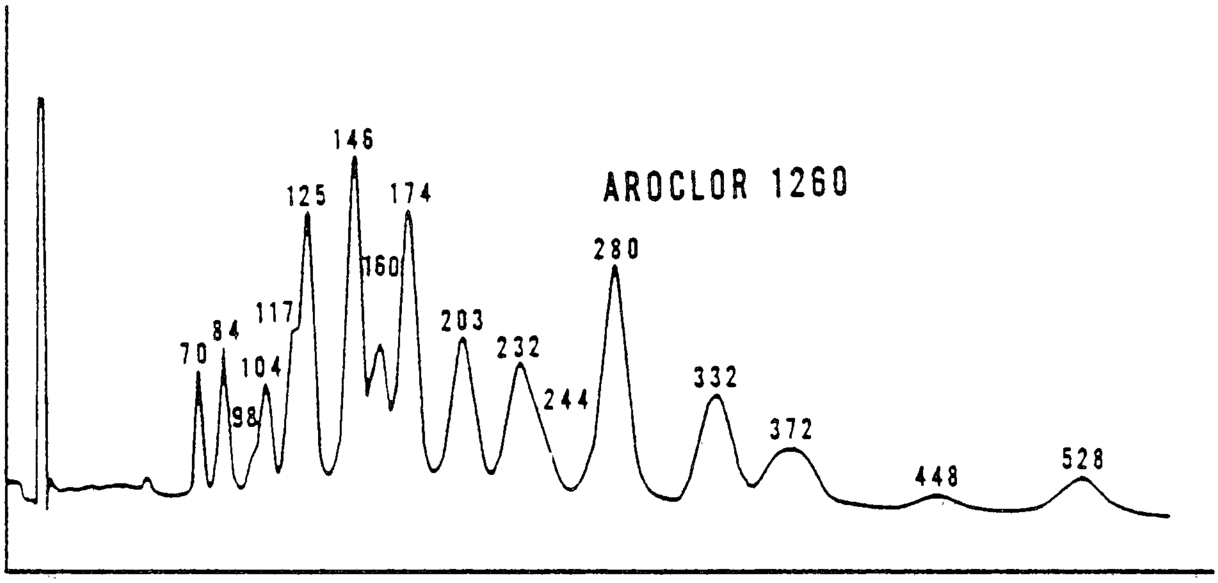


Figure 5. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

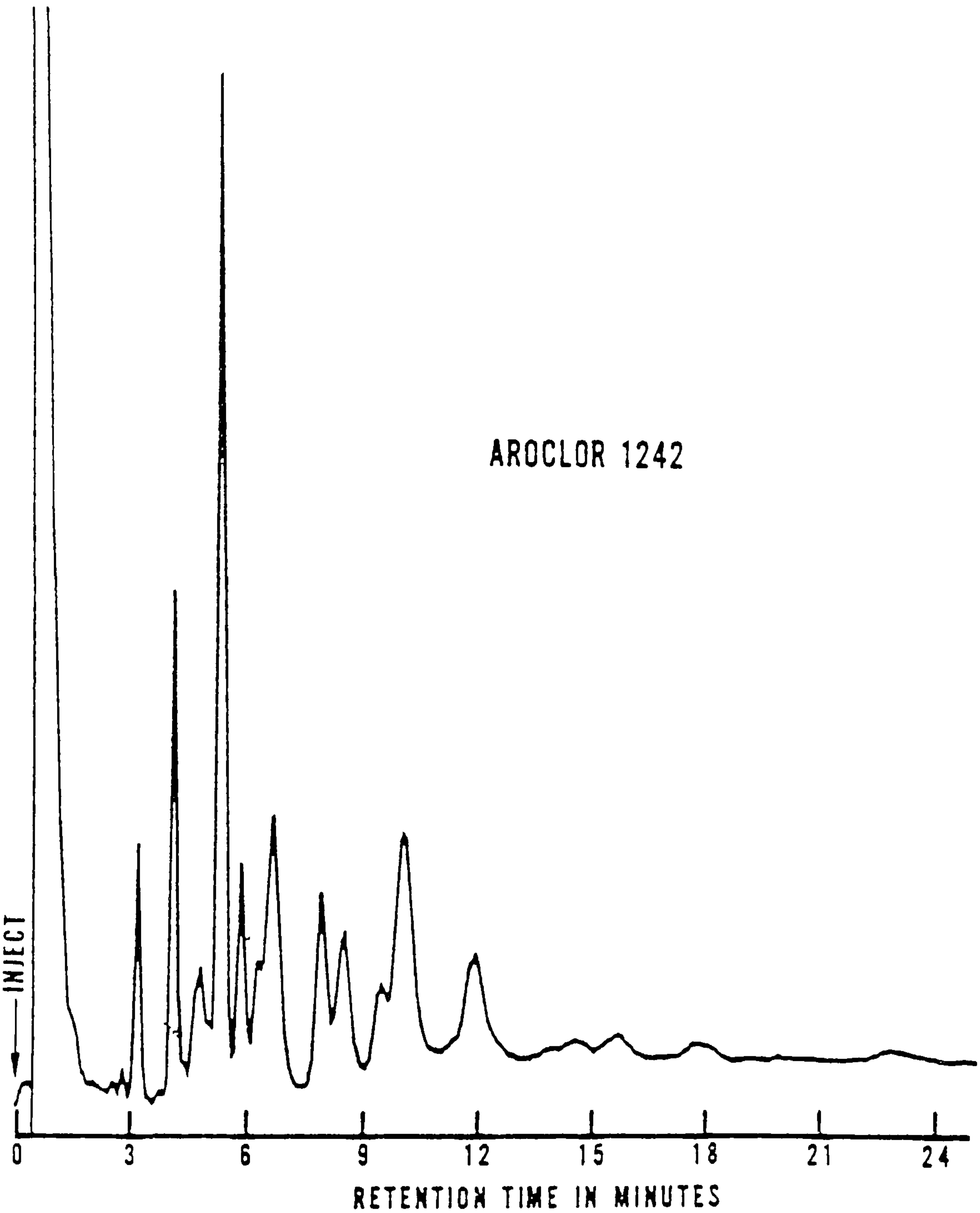


Figure 6. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture

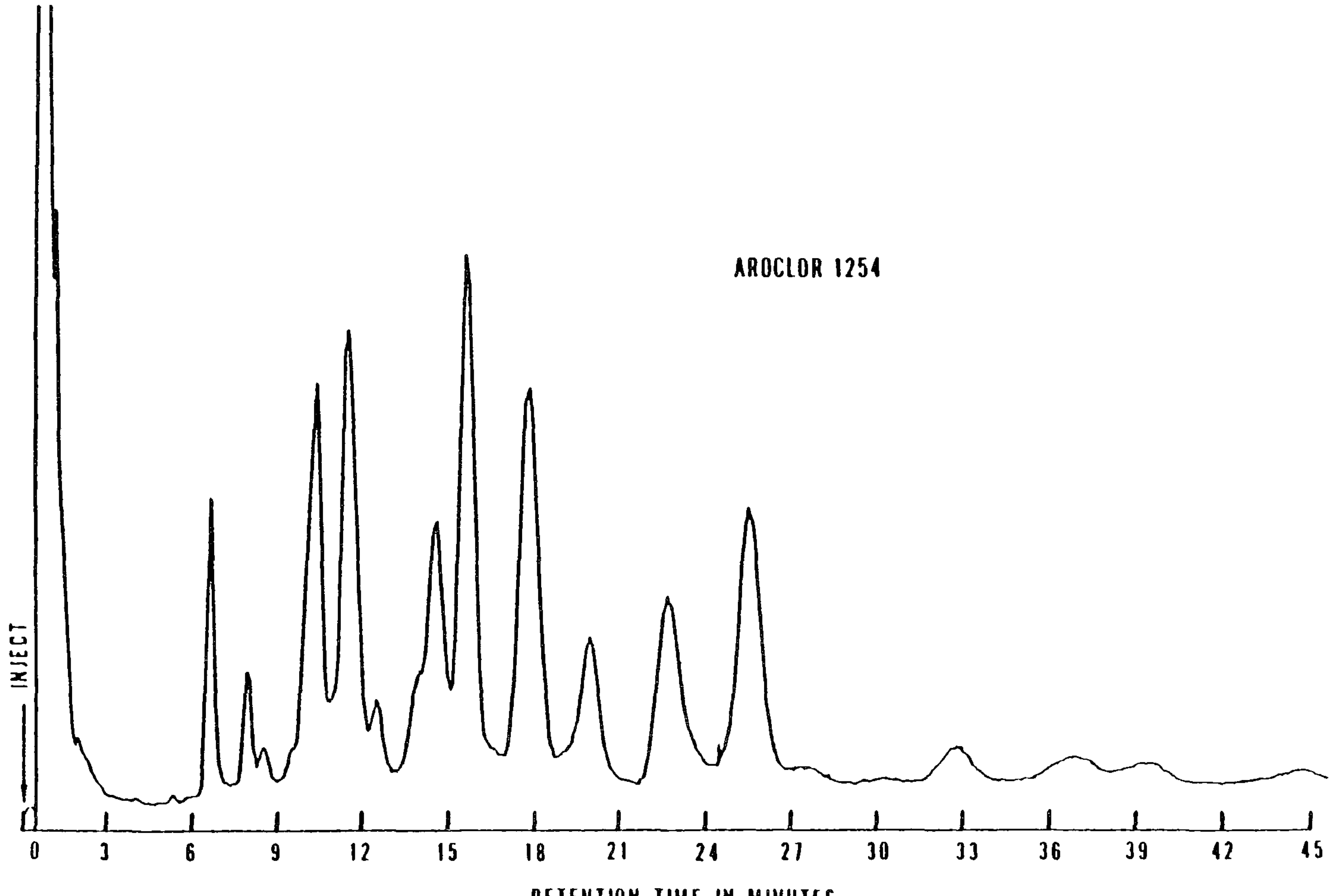


Figure 7. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

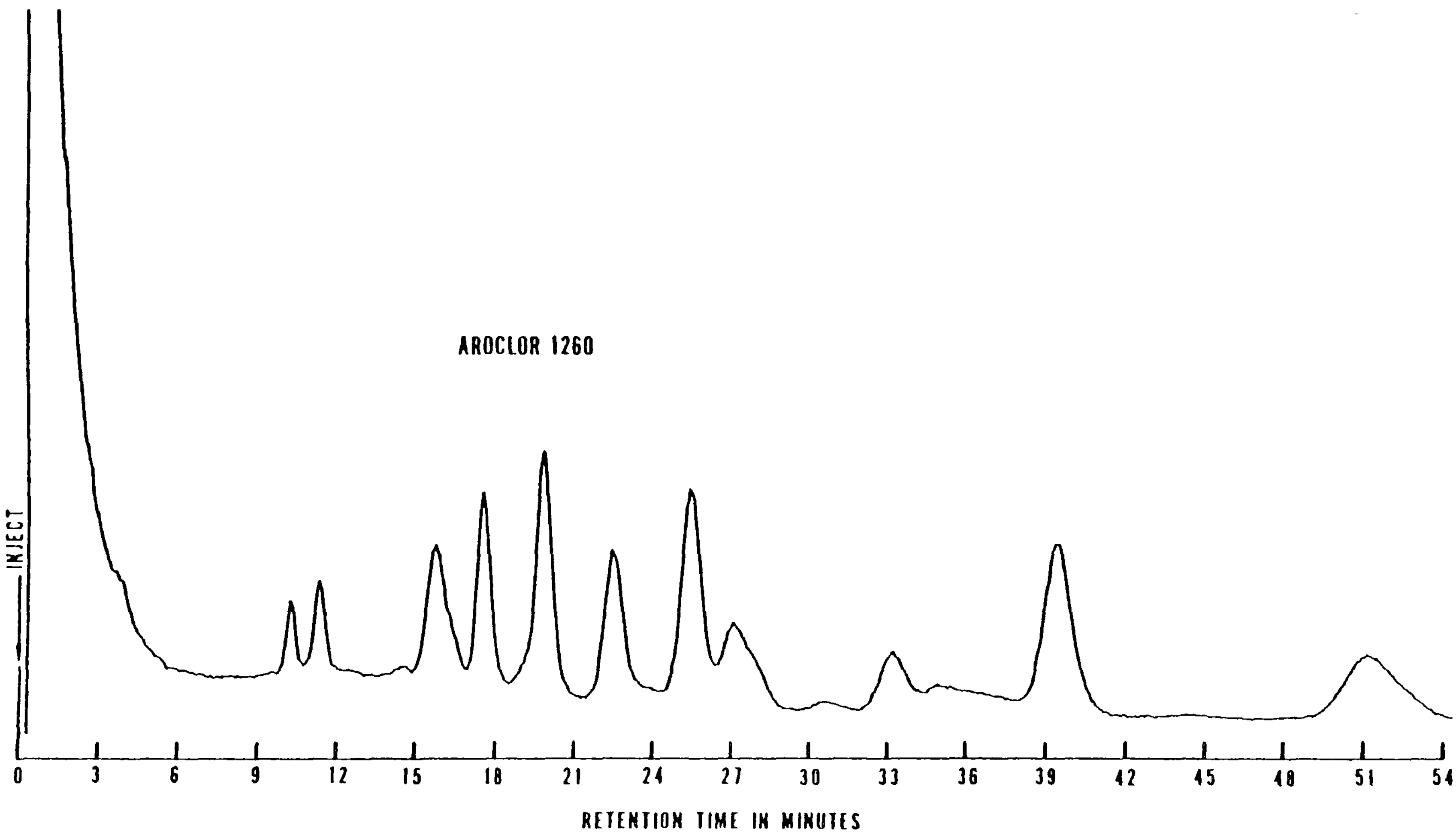


Figure 8. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200C, Detector: Electron Capture.

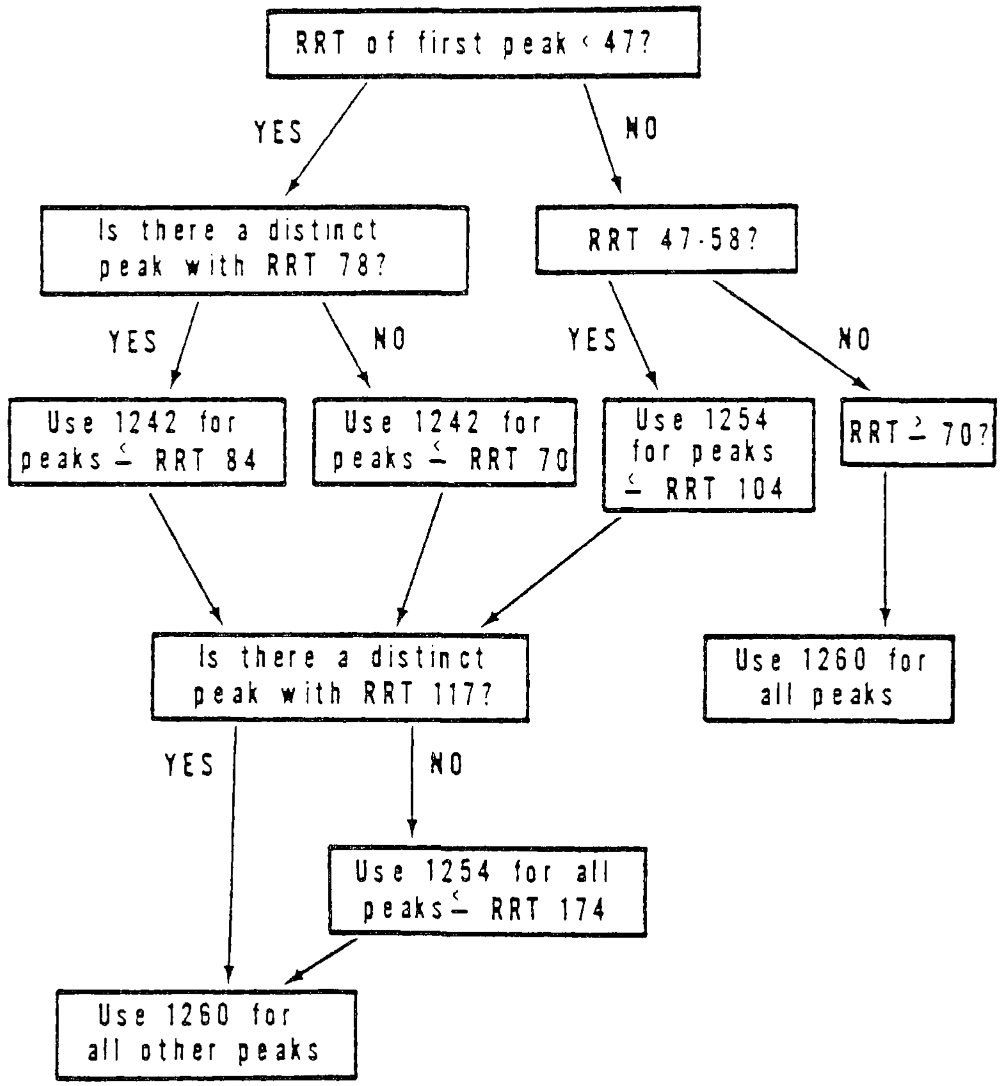


Figure 9. Chromatogram Division Flowchart (8).

☆ U.S. GOVERNMENT PRINTING OFFICE: [illegible]— 657-044/0003

Attachment B

Tentative Method of Testing for Polychlorinated Biphenyls in Water

ENVIRONMENTAL PROTECTION AGENCY
REGION II
EDISON, NEW JERSEY 08817

REPLY TO ATTN OF: 2-SA-TS

DATE: January 22, 1976

SUBJECT: Tentative Method of Test For Polychlorinated Biphenyls in Water.

FROM: Chief, Technical Support Branch

Tentative Method of Test

For Polychlorinated Biphenyls in Water

1. Scope & Application

1.1 This method covers the determination of certain polychlorinated biphenyls (PCB's) including Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260.

1.2 The method covers the analysis of water samples.

1.3 This method used a Finnigan Mass Spectrometer and Systems Industries Data System. Other GC/MS systems could be employed for the same analysis.

2. Applicable References

2.1 O. Hutzinger, S. Safe, V. Zitko, "The Chemistry of PCB's" CRC Press, Cleveland, Ohio 44128 (1974).

2.2 S. Safe & O. Hutzinger, "Mass Spectrometry of Pesticides and Pollutants", CRC Press, Cleveland, Ohio, 1973.

2.3 Methods for Organic Pesticides in Water and Wastewater, EPA, NERC, Cincinnati, Ohio 45268, (1971).

2.4 Current Practice in GC-MS Analysis of Organics in Water, EPA Protection Technology Service, EPA -R2-73-277, August 1973.

2.5 E. J. Bonelli, M.S. Story and J. B. Knight, Dynamic Mass Spectrometry Vol. 2, 177-202, Heyden & Son Ltd., 1971, U.K.

2.6 E. J. Bonelli, Anal. Chem., 44, 603-606 (1972).

2.7 T. A. Bellar & J. J. Lichtenberg, ASTM, STP 573, 206-219 (1975).

2.8 J. W. Eichelberger, L. E. Harris and W. L. Budde, Anal. Chem. 46, 227-232.

2.9 F. W. McLafferty, "Interpretation of Mass Spectra", 2nd Ed., WA Benjamin, Inc., Reading, Mass., 1973.

3. Summary

PCB's are liquid-liquid extracted and the extract concentrated. Identification and quantitation is made by computerized gas chromatograp mass spectrometry. Either electron impact (70 ev) or chemical ionizatio (methane reagent gas) mass spectrometry is employed. The detection limit is approximately 20 ng/l for the PCB mixtures listed in Section 1.1 when analyzing a 100 ul extract from a one liter water sample and operating the C.I. mass spectrometer at 1.0 amp filament current, -2200 V continuous dynode, 10^{-8} A/V, 750 microns reagent gas pressure. In the E.I. mode at 500^{+} ma, -2200 V., 10^{-7} A/V, the detection limit is 200 ng/l. At 10^{-8} A/V, the detection limit is 20 ng/l.

4. Interferences

No interferences are encountered using molecular ion cluster scanning for biphenyl, mono-, di-, etc. chlorobiphenyls and checking isotope intensity ratios.

5. Apparatus & Reagents

5.1 Computerized GC/MS.

5.2 Separatory funnel, 2000 ml, with Teflon stopcock.

5.3 100 ml and 2000 ml graduated cylinders.

5.4 Pesticide grade hexane.

5.5 Pesticide grade methylene chloride.

5.6 Pesticide grade acetone.

5.7 Anhydrous sodium sulfate, granular, reagent grade.

5.8 Sodium chloride, reagent grade.

5.9 Pyrex glass wool.

5.10 Pyrex chromatographic column, approx. 20 mm. o.d., 200 mm long, with Pyrex glass wool plug at bottom.

5.11 Kuderna-Danish (K-D) glassware.

5.11.1 Synder columns, three-ball (macro).

5.11.2 Evaporative flasks, 500 ml.

5.11.3 Receiver ampuls, 4.0 ml graduated.

5.11.4 Receiver ampuls, 2.0 ml, graduated to 0.01 ml from 0.30 to 0.00 ml.

5.11.5 Ampul stoppers.

5.11.6 Beaker, 250 ml.

5.12 Microsyringe, 10 ul.

5.13 PCB mixtures (Aroclor) standards as mentioned in 1.1 above.

6. Extraction of Sample

6.1 Add about 20 gms sodium chloride to a separatory funnel (5.2). Transfer about 1 liter of water sample (measured exactly). Extract the sample twice with 60 ml of methylene chloride-hexane (15% v/v) and once with 60 ml hexane.

6.2 Dry the combined extracts by passing through a 10 cm chromatographic column (5.8) of anhydrous sodium sulfate (previously rinsed with hexane). Collect in K-D flask.

6.3 For trace quantities, concentrate to 1.0 ml in 4.0 ml receiver ampul on steam bath, using dry N_2 stream to reach a volume of about 1 ml.

6.4 Transfer extract (rinsing ampul with 1 ml of hexane) to 2.0 ml ampul and concentrate to 0.10 ml (100 ul) using dry N_2 stream. For larger concentrations of PCB's use a larger volume of extract and/or operate the M.S. at lower sensitivity to avoid signal saturation.

7. Analysis of Extract by Computerized GC/MS

7.1 Gas chromatographic conditions.
Use 6 ft. X 2 mm i.d. glass column, packed with 3% Dexsil 300 GC, OV-1 or OV-101 on 60/80 mesh acid-washed Chromosorb G. Helium carrier gas flow rate of 20 ml/min. inlet (resulting in about 1.5 ml/min. outlet) is used. The column temperature is programmed @ 10°C/min. from 150-280°C (OV-1 coiled column) on from 175-280°C (Dexsil 300 GC U-tube). Charge 3 ul

extract. Allow 75 sec. for solvent to elute. Turn on RF & ionizer & start collecting data. Methane (750 u) is the carrier gas for CI MS.

7.2 E.I. Mass Spectrometer Operating Conditions
70 ev. electron energy
-2200 V continuous dynode
10^{-7} A/V sensitivity (10^{-8} A/V if available)
500^{+} ua (max) filament current

7.3 E.I. Mass Spectrometer Scan Conditions
Mass Range: 153-157; 188-193; 222-227; 256-261; 290-295; 324-331; 358-364; 392-398.
Integration Time: 50; 50; 50; 50; 50; 50; 50; 50
Samples/AMU: 1; 1; 1; 1; 1; 1; 1; 1

7.4 C.I. MS Operating Conditions
750 microns methane reagent gas (optimize signal on MS by using 652 amu of FC-43 on oscilloscope)
-2200 V continuous dynode
1.0 ma filament current

7.5 C.I. Mass Spectrometer Scan Conditions
Same as for E.I. (7.3).

8. Qualitative Identification of PCB's

The presence of PCB mixtures is qualitatively assured from their mass spectra and GC retention data, using the molecular ion region for biphenyl (present in Aroclor 1221 and 1232) and the molecular ion isotope clusters for mono- through heptachlorobiphenyls.
153-157 biphenyl 154M^{+} (EI), 155 (C.I.)
188-193 monochlorobiphenyls
222-227 dichlorobiphenyls
256-261 trichlorobiphenyls
290-296 tetrachlorobiphenyls
324-331 pentachlorobiphenyls
358-361 hexachlorobiphenyl
392-398 heptachlorobiphenyl
The theoretical peak intensities in these molecular ion regions are given in Table A-2, p. 260 of reference 2.9 above. If C.I. (methane) is used, the masses are one greater then for E.I. Identification of the particular Aroclor mixture or even several mixtures can be determined by comparison with standards.

9. Quantitative Determination of PCB's

Once the Aroclor mixture present has been identified (e.g., as Aroclor 1016), a known standard is run and a GC peak present in both (such as the largest Cl_3 biphenyl in the case of 1016) is used for quantitation from total ion intensities in the 256-261 amu region. In the case of a mixture, such as 1016 and 1254, 1254 is first determined from a Cl_3 biphenyl peak not present in 1016. The trichlorobiphenyl peak, mentioned above, is used to determine the 1016, correcting for the 1254 contribution for that peak. Similar approaches are used for other mixtures.
A standard is run before and after each daily batch of samples. It has been found that the total ion intensity over the course of 8 hrs. varies by about ± 5 to 7% from the mean. (2 runs).

10. Minimum Detectable Levels

These are given in the Summary (3).

11. Quality Control Data

In order to assure the validity of the analytical results, samples of laboratory potable water were measured into 1 liter borosilicate bottles closed with aluminum foil-lined screw caps. The water was then spiked with 1016 Aroclor. The PCB mixture was added as an acetone solution.

Results

Sample No.	Date	PCB-1016, ug/l Added	Found	Recovery Per Cent of Added Amount
B	8/21	0	<1	-
L	8/21	5.4	6.4	119
I	8/21	51.4	53	103
H	8/21	446	447	100
H-2	8/26	5.9	6.6	112
I-2	8/26	91.2	88.5	97
L-2	8/26	12.9	11.4	88

Triplicate samples collected at GE Water Intake I on 8/26/75 gave the following results:

Station	Date Collected	PCB ug/l
Intake I	8/25/75	16
		15
		15

12. Glassware Preparation

1. All glassware is washed 3 times in an automatic washer, first with a detergent water solution, then twice with distilled water and dried.

2. All glassware is then carefully rinsed once with acetone and once with hexane.

3. The drying agent, reagent grade granular anhydrous Na_2SO_4 is dried for a minimum of 24 hours at 105°C. It is kept at this temperature prior to usage. Only materials used for pesticide and PCB analyses are kept in this oven.

4. The glass wool and the Na_2SO_4 are rinsed with hexane and stored at 105°C.

B. F. Dudenbostel
Chemist

Attachment C

Determination of CO Emissions from Stationary Sources

METHOD 10—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 *Principle.* An integrated or continuous gas sample is extracted from a sampling point and analyzed for carbon monoxide (CO) content using a Luft-type nondispersive infrared analyzer (NDIR) or equivalent.

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

2. *Range and sensitivity.*

2.1 *Range.* 0 to 1,000 ppm.

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

3. *Interferences.* Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. *Precision and accuracy.*

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

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

5. *Apparatus.*

5.1 *Continuous sample* (Figure 10–1).

5.1.1 *Probe.* Stainless steel or sheathed Pyrex[1] glass, equipped with a filter to remove particulate matter.

5.1.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2 *Integrated sample* (Figure 10–2).

5.2.1 *Probe.* Stainless steel or sheathed Pyrex glass, equipped with a filter to remove particulate matter.

5.2.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2.3 *Valve.* Needle valve, or equivalent, to to adjust flow rate.

5.2.4 *Pump.* Leak-free diaphragm type, or equivalent, to transport gas.

5.2.5 *Rate meter.* Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per min. (0.035 cfm).

5.2.6 *Flexible bag.* Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft³). Leak-test the bag in the laboratory before using by evacuating bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

5.2.7 *Pitot tube.* Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with the time or a sample traverse is conducted.

5.3 *Analysis* (Figure 10–3).

5.3.1 *Carbon monoxide analyzer.* Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

5.3.2 *Drying tube.* To contain approximately 200 g of silica gel.

5.3.3 *Calibration gas.* Refer to paragraph 6.1.

5.3.4 *Filter.* As recommended by NDIR manufacturer.

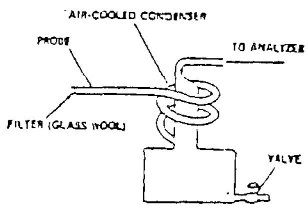


Figure 10-1. Continuous sampling train.

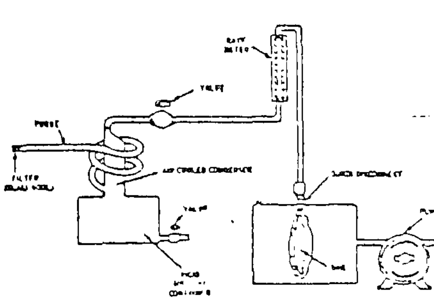


Figure 10-2. Integrated gas-sampling train.

5.3.5 CO_2 *removal tube.* To contain approximately 500 g of ascarite.

5.3.6 *Ice water bath.* For ascarite and silica gel tubes.

5.3.7 *Valve.* Needle valve, or equivalent, to adjust flow rate.

5.3.8 *Rate meter.* Rotameter or equivalent to measure gas flow rate of 0 to 1.0 liter per min. (0.035 cfm) through NDIR.

5.3.9 *Recorder (optional).* To provide permanent record of NDIR readings.

6. *Reagents.*

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

6.1 *Calibration gases.* Known concentration of CO in nitrogen (N_2) for instrument span, prepurified grade of N_2 for zero, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.

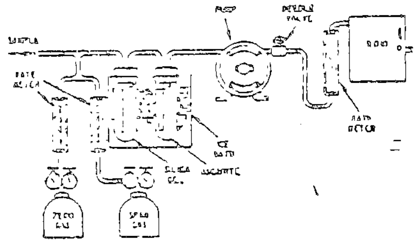


Figure 10-1. Analytical equipment.

6.2 *Silica gel.* Indicating type, 6 to 16 mesh, dried at 175° C (347° F) for 2 hours.

6.3 *Ascarite.* Commercially available.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Continuous sampling.* Set up the equipment as shown in Figure 10-1 making sure all connections are leak free. Place the probe in the stack at a sampling point and purge the sampling line. Connect the analyzer and begin drawing sample into the analyzer. Allow 5 minutes for the system to stabilize, then record the analyzer reading as required by the test procedure. (See § 7.2 and 8). CO_2 content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 *Integrated sampling.* Evacuate the flexible bag. Set up the equipment as shown in Figure 10-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures (36 FR 24886), or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

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

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

TABLE 10-1.—*Field data*

Location ______	Comments:
Test ______	
Date ______	
Operator ______	

Clock time	*Rotameter setting, liters per minute (cubic feet per minute)*

9. *Calculation—Concentration of carbon monoxide.* Calculate the concentration of carbon monoxide in the stack using equation 10-1.

$$C_{CO_{stack}} = C_{CO_{NDIR}}(1 - F_{CO_2}) \qquad \text{equation 10-1}$$

where:

$C_{CO_{stack}}$ = concentration of CO in stack, ppm by volume (dry basis).

$C_{CO_{NDIR}}$ = concentration of CO measured by NDIR analyzer, ppm by volume (dry basis).

F_{CO_2} = volume fraction of CO_2 in sample, i.e., percent CO_2 from Orsat analysis divided by 100.

10. *Bibliography.*

10.1 McElroy, Frank, The Intertech NDIR–CO Analyzer, Presented at 11th Methods Conference on Air Pollution, University of California, Berkeley, Calif., April 1, 1970.

10.2 Jacobs, M. B., et al., Continuous Determination of Carbon Monoxide and Hydrocarbons in Air by a Modified Infrared Analyzer, J. Air Pollution Control Association, 9(2):110–114, August 1959.

10.3 MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Technical Products Division, Pittsburgh, Pa.

10.4 Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instruments, Inc., Beckman Instructions 1635–B, Fullerton, Calif., October 1967.

10.5 Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton, N.J.

10.6 UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, West Virginia.

ADDENDA

A. Performance Specifications for NDIR Carbon Monoxide Analyzers.

Range (minimum)	0–1000ppm.
Output (minimum)	0–10mV.
Minimum detectable sensitivity	20 ppm.
Rise time, 90 percent (maximum)	30 seconds.
Fall time, 90 percent (maximum)	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	10% in 8 hours.
Precision (minimum)	± 2% of full scale.
Noise (maximum)	± 1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO_2—1000 to 1, H_2O—500 to 1.

B. *Definitions of Performance Specifications.*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full scale—The maximum measuring limit for a given range.

Minimum detectable sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Time to 90 percent response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

METHOD 11—DETERMINATION OF HYDROGEN SULFIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 *Principle.* Hydrogen sulfide (H_2S) is collected from the source in a series of midget impingers and reacted with alkaline cadmium hydroxide [$Cd(OH)_2$] to form cadmium sulfide (CdS). The precipitated CdS is then dissolved in hydrochloric acid and absorbed in a known volume of iodine solution. The iodine consumed is a measure of the H_2S content of the gas. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species.

1.2 *Applicability.* This method is applicable for the determination of hydrogen sulfide emissions from stationary sources only when specified by the test procedures for

determining compliance with t… performance standards. …

2. *Apparatus.*

2.1 *Sampling train.* …

2.1.1 *Sampling line*—6- to 7-… Teflon[1] tubing to connect sam… sampling valve, with provision… to prevent condensation. A pr… ing valve prior to the Teflon … may be required depending… stream pressure.

2.1.2 *Impingers*—Five midge… each with 30-ml capacity, or eq…

2.1.3 *Ice bath container*—To … sorbing solution at a constant t…

2.1.4 *Silica gel drying tube*… pump and dry gas meter.

2.1.5 *Needle valve, or equivale*… steel or other corrosion resistan… adjust gas flow rate.

2.1.6 *Pump*—Leak free, diaph… equivalent, to transport gas. (… if sampling stream under posit…

2.1.7 *Dry gas meter*—Sufficie… to measure sample volume to … cent.

2.1.8 *Rate meter*—Rotameter, … to measure a flow rate of 0 to… minute (0.1 ft³/min).

2.1.9 *Graduated cylinder*—25…

2.1.10 *Barometer*—To measure… pressure within ±2.5 mm (0.1…

2.2 *Sample Recovery.*

2.2.1 *Sample container*—500-… pered iodine flask.

2.2.2 *Pipette*—50-ml volumet…

2.2.3 *Beakers*—250 ml. …

2.2.4 *Wash bottle*—Glass.

2.3 *Analysis.*

2.3.1 *Flask*—500-ml glass-sto… flask.

2.3.2 *Burette*—One 50 ml.

2.3.2 *Flask*—125-ml conical.

3. *Reagents.*

3.1 *Sampling.*

3.1.1 *Absorbing solution*—C… droxide ($Cd(OH)_2$)—Mix 4.3 g c… fate hydrate ($3\ CdSO_4.8H_2O$) … sodium hydroxide (NaOH) in 1… tilled water (H_2O). Mix well.

Note: The cadmium hydroxi… this mixture will precipitate as… pension. Therefore, this soluti… thoroughly mixed before using… even distribution of the cadmiu…

3.1.2 *Hydrogen peroxide, 3 per*… 30 percent hydrogen peroxide… as needed. Prepare fresh daily.

3.2 *Sample recovery.*

3.2.1 *Hydrochloric acid soluti… percent by weight*—Mix 230 m…

[1] Mention of trade names or s… ucts does not constitute endors… Environmental Protection Agen…

Attachment D

Gas Analysis for CO_2, O_2, Excess Air, and Dry Molecular Weight

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, N.C. (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. American Society of Mechanical Engineers, New York, N.Y. 1959.

7. ASHRAE Handbook of Fundamentals. 1972. p. 208.

8. Annual Book of ASTM Standards, Part 26. 1974. p. 64.

9. Vollaro, R. F. Guidelines for Type S Pitot Tube Calibration. U.S. Environmental Protection Agency, Research Triangle Park, N.C. (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, N.C. 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, N.C. October 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, N.C. November 1976.

13. Vollaro, R. F. An Evaluation of Single-Velocity Calibration Techniques as a Means of Determining Type S Pitot Tube Coefficients. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, N.C. 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, N.C. November 1976.

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

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

1. *Principle and Applicability*

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

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

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

2. *Apparatus*

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

2.1 Grab Sampling (Figure 3–1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other 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.

---

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

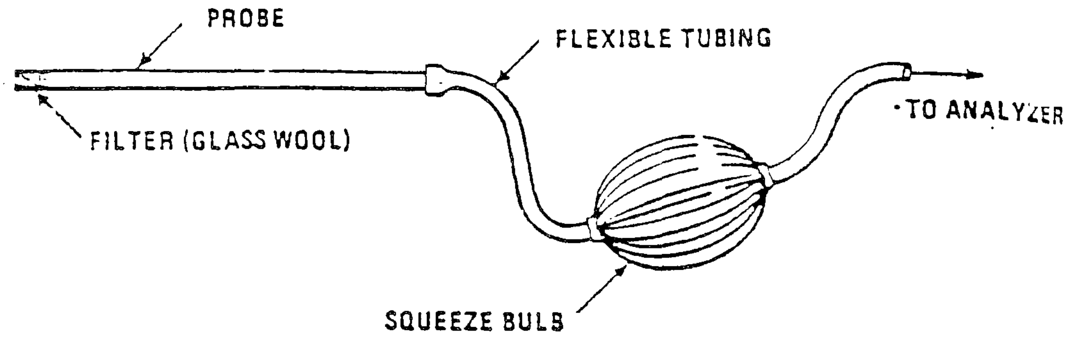


Figure 3-1. Grab-sampling train.

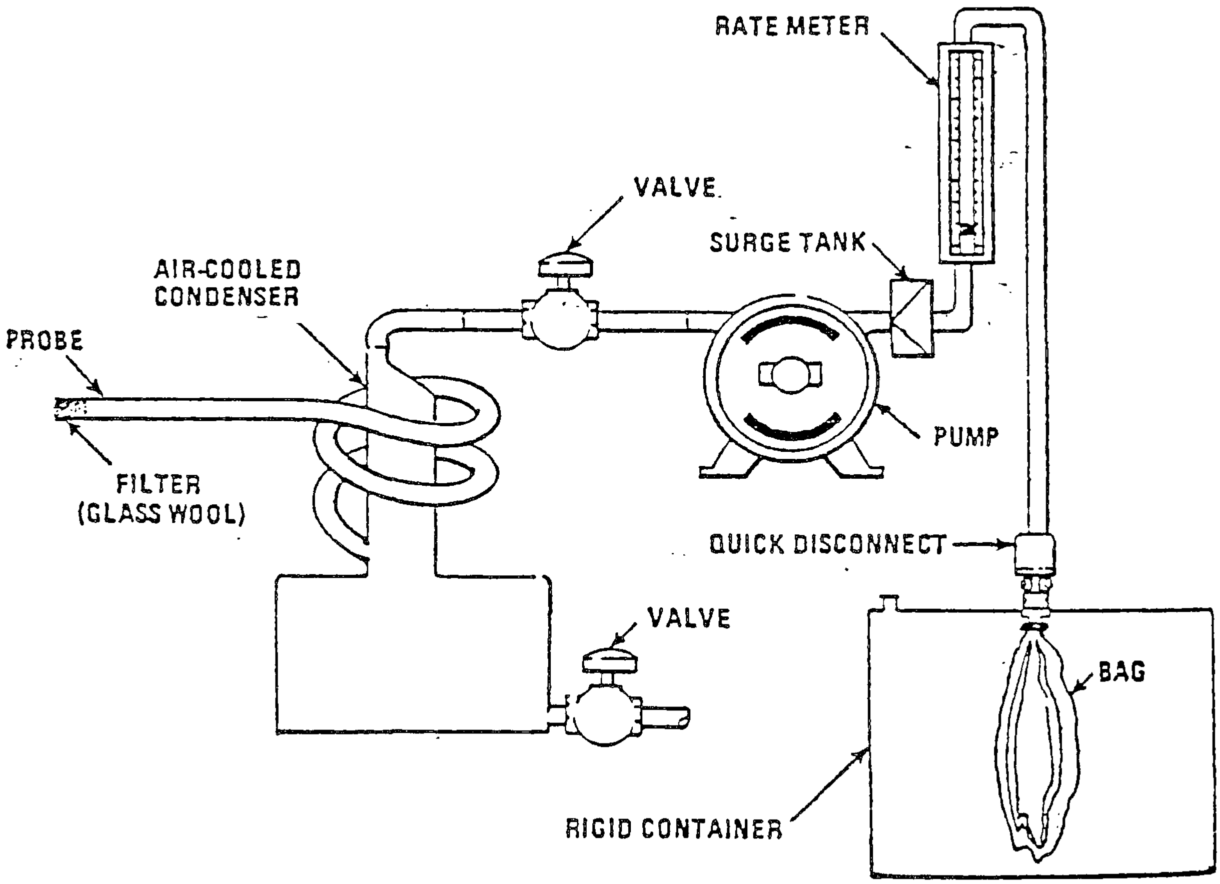


Figure 3-2. Integrated gas-sampling train.

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 cm³/min is suggested.

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

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

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 28 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 Administrator.

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

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

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

3.2 Single-Point, Integrated Sampling and Analytical Procedure.

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

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

3.2.3 Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft³) of sample gas is recommended; however, smaller volumes may be collected, if desired.

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

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

3.3 Multi-Point, Integrated Sampling and Analytical Procedure.

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

3.3.2 Follow the procedures outlined in Sections 3.2.2 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 Administrator. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

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

4.1 *Single-Point, Grab Sampling and Analytical Procedure.*

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

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

TIME	TRAVERSE PT.	Q 1pm	% DEV.[a]
	AVERAGE		

$$^{a}\% \text{ DEV} = \left(\frac{Q - Q_{avg}}{Q_{avg}}\right) 100 \quad (\text{MUST BE} \leq 10\%)$$

Figure 3-3. Sampling rate data.

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 Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 30 liters (1.00 ft³) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-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 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 Administrator.

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

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).
%EA = Percent excess air.
$\%CO_2$ = Percent CO_2 by volume (dry basis).
$\%O_2$ = Percent O_2 by volume (dry basis).
%CO = Percent CO by volume (dry basis).
$\%N_2$ = Percent N_2 by volume (dry basis).
0.264 = Ratio of O_2 to N_2 in air, v/v.
0.280 = Molecular weight of N_2 or CO, divided by 100.
0.320 = Molecular weight of O_2 divided by 100.
0.440 = Molecular weight of CO_2 divided by 100.

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

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

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 oven or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil, and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternate methods, subject to approval of the Administrator, are required.

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

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

Equation 3-2

NOTE.—The above equation does not consider argon in air (about 0.9 percent, 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 Administrator.

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 Plastic Bags. Journal of the American Industrial Hygiene Association. 25:291-297. 1964.

3. Burrell Manual for Gas Analysts. 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):21-26. August, 1976.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

1. Principle and Applicability

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

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

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

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, U.S. Environmental Protection Agency, to be capable of yielding results within 1 percent H_2O of the reference method.

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

2. Reference Method

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

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

Attachment E

Determination of Total Polychlorinated Biphenyl (PCB) Emissions from Industrial, Sewage Sludge, and Municipal Refuse Incinerators (Draft Method)

PART A. INDUSTRIAL, SEWAGE SLUDGE, AND MUNICIPAL REFUSE INCINERATORS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The total PCBs in the train are determined by perchlorination to decachlorobiphenyl (DCB) and gas chromatographic determination of the DCB.

1.2 Applicability. This method is applicable for the determination of PCB emissions (both vaporous and particulate) from industrial, sewage sludge, and municipal refuse incinerators.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. However, the sensitivity of the total method as described here is about 10 ng DCB for each analytical replicate.

3. Interferences

Excessive quantities of acid-resistant organics may cause significant interferences obscuring the analysis of DCB in the perchlorinated extracts. Biphenyl, although unlikely to be present in samples from combustion sources, can form DCB in the perchlorination processes.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Adhesives must not be used to hold TFE® liners on lids, and lubricating and sealing greases must not be used on any sample exposed portions of the sampling train.

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95%.

5. Apparatus

5.1 Sampling Train. See Figure A-1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train. Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle--Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30 degrees and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

5.1.2 Probe liner--Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases; such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Administrator. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube--Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge--Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However,

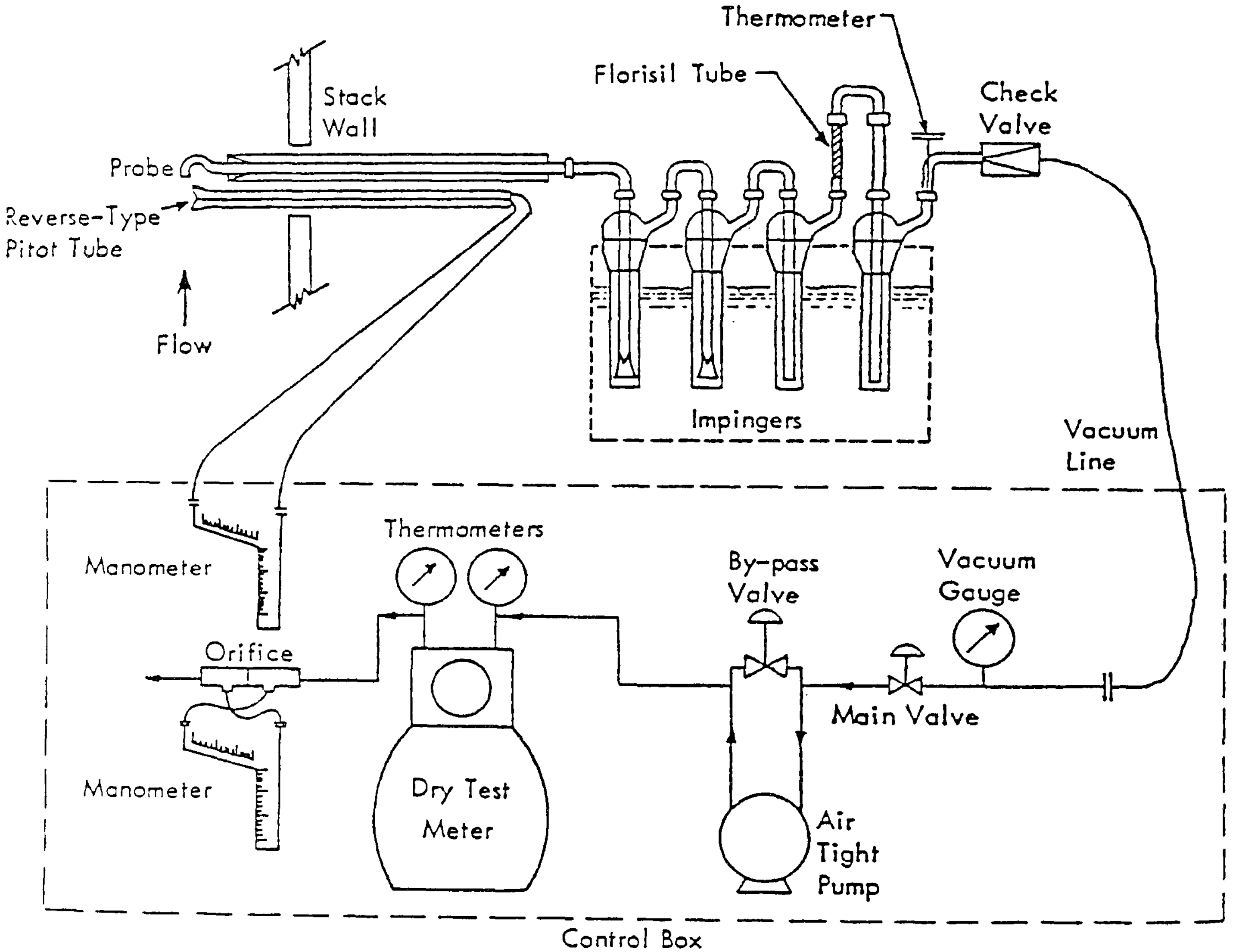


Figure A-1. PCB Sampling Train for Incinerators micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Administrator may be used when conditions warrant.

5.1.5 Impingers--Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure A-1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

5.1.6 Solid adsorbent tube--Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure A-2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system--Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer--Mercury, aneroid, or other barometers 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 weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Sample Recovery

5.2.1 Ground glass caps--To cap off adsorbent tube and the other sample exposed portions of the train.

5.2.2 Teflon FEP® wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.2.3 Sample storage containers--Glass bottles, 1 liter, with TFE®-lined screw caps.

5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.

5.2.5 Aluminum foil--Heavy duty.

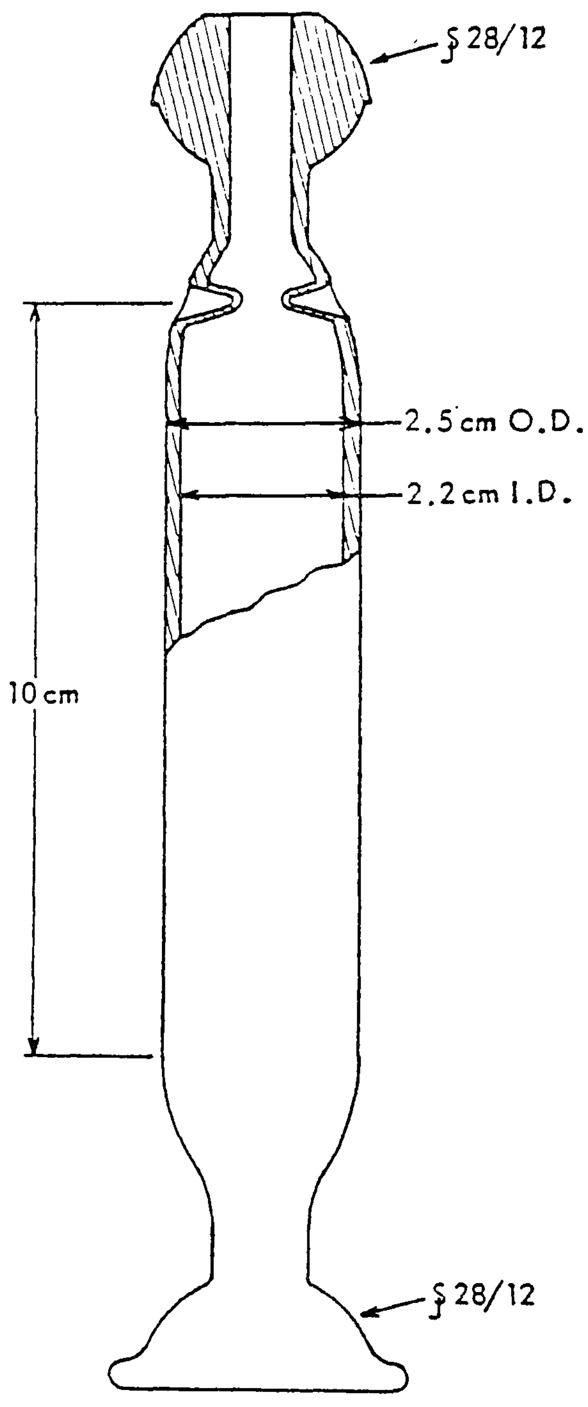


Figure A-2. Florisil Adsorbent Tube

5.2.6 Metal can--To recover used silica gel.

5.3 <u>Analysis</u>

5.3.1 Glass Soxhlet extractors--40 mm ID complete with 45/50 $\mathfrak{F}$ condenser, 24/40 $\mathfrak{F}$ 250 ml round bottom flask, heating mantle for 250 ml flask, and power transformer.

5.3.2 Teflon FEP wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.3.3 Separatory funnel--1,000 ml with TFE® stopcock.

5.3.4 Kuderna-Danish concentrators--500 ml.

5.3.5 Steam bath.

5.3.6 Separatory funnel--50 ml with TFE® stopcock.

5.3.7 Volumetric flask--25.0 ml, glass.

5.3.8 Volumetric flask--5.0 ml, glass.

5.3.9 Culture tubes--13 x 100 mm, glass with TFE®-lined screw caps.

5.3.10 Pipette--5.0 ml glass.

5.3.11 Aluminum block--Drilled to support culture tubes while heating.

5.3.12 Hot plate--Capable of heating to 200°C.

5.3.13 Teflon®-glass syringe--1 ml, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.3.14 Syringe--10 µl, Hamilton 701N or equivalent.

5.3.15 Gas chromatograph--Fitted with electron capture detector capable of operation at 300°C and with 2 mm ID x 1.8 mm glass column packed with 3% OV-210 on 100/120 mesh inert support (e.g., Supelcoport®).

5.3.16 Electric muffle furnace--Capable of heating to 650°C.

5.3.17 Electric oven--Capable of heating to 150°C.

5.3.18 Disposable glass pipettes with bulbs--To aid transfer of the extracts.

5.3.19 Porcelain casserole--Capable of withstanding temperatures as high as 650°C.

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Co., 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water--Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel--Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Sample Recovery

6.2.1 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3 Analysis

6.3.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.3 Water--Deionized and then glass-distilled, stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.3.4 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.3.5 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.3.6 Antimony pentachloride ($SbCl_5$)--Baker Analyzed Reagent or equivalent.

6.3.7 Hydrochloric acid (HCl) solution--ACS reagent grade or equivalent, 50% in water.

6.3.8 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.3.9 Decachlorobiphenyl--RFP Corp., No. RPC-60, or equivalent.

6.3.10 Compressed nitrogen--Prepurified.

6.3.11 Carborundum boiling stones--Hengar Co. No. 133-B or equivalent, rinsed with hexane.

7. Procedure

Caution: Section 7.1.1 should be done in the laboratory.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularily contamination problems.

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

7.1.1.1 Cleaning glassware. All glass parts of the train upstream of and including the adsorbent tube, 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." 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.

7.1.1.2 Solid adsorbent tube. Weigh 7.5 g of Florisil, activated within the last 30 days and still warm from storage in a 110°C oven, into the adsorbent tube (pre-rinsed with hexane) with a glass wool plug in the downstream end. Place a second glass wool plug in the tube to hold the sorbent in the tube. Cap both ends of the tube with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Determine the molecular weight of the stack gases using Method 3.

Select a nozzle size based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. 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.

Select a suitable probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a sampling time appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

It is recommended that a buzzer-timer be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

In some circumstances, e.g., short batch processes, it may be necessary to sample through two or more batches to obtain sufficient sample volume. In these cases, sampling should cease during loading/unloading of the furnace.

7.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, rinse all parts of the train upstream of the adsorbent tube with hexane.

Mark the probe with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

Place 200 ml of water in each of the first two impingers, and leave the third impinger empty. CAUTION: do not use sealant greases in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 10.1. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

Assemble the train as shown in Figure A-1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Place crushed ice around the impingers.

7.1.4 Leak check procedure--After the sampling train has been assembled, turn on and set (if applicable) the probe heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of bypass valve. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) 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 and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Train operation--During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained. During the run, do not change the nozzle or any other part of the train in front of and including the Florisil tube.

For each run, record the data required on the data sheets. An example is shown in Figure A-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Be sure to level and zero the manometer.

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

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

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

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator. To minimize chance of extracting deposited material, be careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

FIELD DATA

PLANT ____________
DATE ____________
SAMPLING LOCATION ____________
SAMPLE TYPE ____________
RUN NUMBER ____________
OPERATOR ____________
AMBIENT TEMPERATURE ____________
BAROMETRIC PRESSURE ____________
STATIC PRESSURE, (P_s) ____________
FILTER NUMBER (s) ____________

PROBE LENGTH AND TYPE ____________
NOZZLE I.D. ____________
ASSUMED MOISTURE, % ____________
SAMPLE BOX NUMBER ____________
METER BOX NUMBER ____________
METER $\Delta H_@$ ____________
C FACTOR ____________
PROBE HEATER SETTING ____________
HEATER BOX SETTING ____________
REFERENCE Δp ____________

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY ________ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
					DESIRED	ACTUAL		INLET ($T_{m\ in}$), °F	OUTLET ($T_{m\ out}$), °F			

COMMENTS

Figure A-3. Field Data Sheet

EPA (Dur) 235
4/72

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during a test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.* Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

7.1.6 Blank train--For each series of test runs, set up a blank train in a manner identical to that described above, but with the nozzle capped with aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Section 7.2.

7.2 Sample recovery. 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. Cap off the inlet to the train with a ground glass cap.

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

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

7.2.1 Adsorbent tube--Remove the Florisil tube from the train and cap it off with ground glass caps.

---

* With acceptability of the test run to be based on the same criterion as in 7.1.4.

7.2.2 Sample container No. 1--Remove the first three impingers. Wipe off the outside of each impinger to remove excessive water and other debris, weigh (stem included), and record the weight on data sheet. Pour the contents directly into container No. 1 and seal.

7.2.3 Sample container No. 2--Rinse each of the first three impingers sequentially first with 30 ml acetone and then with 30 ml hexane, and put the rinses into container No. 2. Quantitatively recover material deposited in the probe using 100 ml acetone and then 100 ml hexane and add these rinses to container No. 2 and seal.

7.2.4 Silica gel container--Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Transfer the contents to the used silica gel can.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with 5 ml acetone and then with 15 ml hexane and put these rinses into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml on a steam bath and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50-ml separatory funnel and set the funnel aside.

7.3.1.2 Sample container No. 1. Transfer the aqueous sample to a 1,000-ml separatory funnel. Rinse the container with 20 ml acetone and then with two 20-ml portions of hexane, adding the rinses to the separatory funnel.

Extract the sample with three 100 ml portions of hexane, transferring the sequential extracts to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil extract. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

7.3.1.3 Sample container No. 2. Transfer the organic solution into a 1,000 ml separatory funnel. Rinse the container with two 20 ml portions of hexane and add the rinses to the separatory funnel. Wash the sample with three 100 ml portions of water. Discard the aqueous layer and transfer the organic layer to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil and impinger extracts.

7.3.2 Extract cleanup--Clean the combined extracts (in 50 ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples" Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25 ml volumetric flask and dilute to volume with hexane. Pipette three 5.0 ml aliquots into culture tubes for perchlorination. Retain the remaining 10 ml for later verification, if required (see Section 10.2).

7.3.3 Extract perchlorination--Evaporate the aliquots in the culture tubes just to dryness with a gentle stream of dry nitrogen. If the aliquots will not evaporate to dryness, refer to Section 10.3 concerning special cases. Add 0.2 ml antimony pentachloride with a 1 ml glass-TFE® syringe and seal the tube with a TFE®-lined screw cap. Heat the reaction mixture to 160°C for 2 hr by placing the tube in a hole in an aluminum block on a hot plate.

Allow the tube to cool to ambient room temperature before adding about 2 ml of 50% HCl in water to destroy residual antimony pentachloride. This is a convenient "stopping point" in the perchlorination procedure.

Extract the reaction mixture by adding about 1 ml hexane to the tube, shake, and allow layers to separate. Remove the upper hexane layer with a disposable pipette and filter through a micro column of anhydrous sodium sulfate directly into a 5 ml volumetric flask. Repeat the extraction three times for a total of four extractions. Dilute the extract to volume with hexane.

7.3.4 PCB determination--Assay the perchlorinated extracts for decachlorobiphenyl (DCB) by gas chromatographic comparison with DCB standard solutions and correct this result for the DCB concentration determined for the blank train. (Column temperature and carrier gas flow parameters of 240°C and 30 ml/min, are typically appropriate. The concentrations of the standard solutions should allow fairly close comparison with DCB in the sample extracts. Standards near 25 to 50 picograms/microliter may be appropriate.)

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than ± 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration--The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the DCB standard.

9. Calculations

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

9.1 Nomenclature

G_n = Corrected weight of DCB in nth perchlorinated aliquot (n = 1, 2, 3), µg.

G_s = Total weight of PCBs (as DCB) in sample, µg.

C_s = Concentration of PCBs in stack gas, µg/m^3, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

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

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

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 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/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

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

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml. volume of water collected equals the weight increase in grams times 1 ml/gram

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

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

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

V_t = Total volume of sample, ml.

V_s = Stack gas velocity, calculated by EPA Method 2, m/sec (ft/sec).

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

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total Sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure A-3).

9.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation A-1).

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

Equation A-1

where $K = 0.3855$ °K/mm Hg for metric units

$= 17.65$ °R/in. Hg for English units

9.4 Volume of water vapor

$$V_{w(std)} = V_{1c} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K\, V_{1c}$$

Equation A-2

where $K = 0.00134\ m^3/ml$ for metric units

$= 0.0472\ ft^3/ml$ for English units

9.5 Moisture content

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

Equation A-3

If the liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

9.6 Concentration

9.6.1 Calculate the total PCB residue (as DCB) in the sample from the weights of DCB in the perchlorinated aliquots according to Equation A-4.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3} \qquad \text{Equation A-4}$$

9.6.2 Concentration of PCBs (as DCB) in stack gas. Determine the concentration of PCBs in the stack gas according to Equation A-5.

$$C_s = K \frac{G_s}{V_{m(std)}} \qquad \text{Equation A-5}$$

where $K = 35.31\ ft^3/m^3$

9.7 Isokinetic variation

9.7.1 Calculations from raw data.

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

Equation A-6

where $K = 0.00346$ mm $Hg\text{-}m^3/ml\text{-}^\circ K$ for metric units

$= 0.00267$ in. $Hg\text{-}ft^3/ml\text{-}^\circ R$ for English units

9.7.2 Calculations from intermediate values.

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

$$= K \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})} \qquad \text{Equation A-7}$$

where $K = 4.323$ for metric units

$= 0.0944$ for English units

9.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If 90% < I < 110%, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results.

10. Special Cases

10.1 Sampling moisture saturated or supersaturated stack gases. One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

10.2 PCB verification. It is recommended that an unperchlorinated aliquot from at least one sample be subjected to GC/MS examination to verify that PCB isomers are present.

To accomplish this, the unperchlorinated portion of each extract is first screened by GC with the same chromatographic system used for DCB determination except for a cooler column temperature, typically 165 to 200°C. The elution patterns are compared with those of commercial PCB mixtures (in hexane solution) to determine the most similar mixture.

After determining what PCB isomers are possible present, the sample is examined by GC/MS using multiple ion selection techniques for ions characteristic of the molecular clusters of the PCBs possibly present.

10.3 Evaporation of extracts for perchlorination. For cases where the extract will not evaporate to dryness or excessive PCB loss by volatilization is suspected, the hexane may be removed by azeotrophic evaporation from the hexane/chloroform mixture.

Add 3 ml of chloroform to the aliquot in the culture tube. Add a boiling chip and concentrate by slow boiling in a water bath to 1 ml. Repeat the chloroform addition and evaporation three times in order to remove all residual hexane. Then further concentrate (slowly) to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C or the solvent be evaporated to dryness. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of solvent level with another reaction vial containing 0.1 ml of chloroform. When a volume of 0.1 ml is achieved, cap the reaction vial immediately and allow to cool. Proceed with the perchlorination as described in Section 7.3.3.

11. References

Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

1973 Annual Book of ASTM Standards, Part 23, Designation: D 1179-72.

Thompson, J. F., Ed., "Analysis of Pesticide Residues in Human and Environmental Samples," Environmental Protection Agency, Research Triangle Park, N.C., 1974.

Attachment F

Determination of Nitrogen Oxide Emissions from Stationary Sources

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

Procedure

4.1 Sampling.

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

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

With the probe disconnected, place a vacuum gauge at the inlet to the bubbler and pull a vacuum of 250 mm (10 in.) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end to prevent back flow of the impinger fluid.

Other leak check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency. The procedure used in Method 5 is not suitable for diaphragm pumps.

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

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

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

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

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

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

5. *Calibration*

5.1 Metering System.

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

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

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

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

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

5.4 Barometer. Calibrate against a mercury barometer.

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

6. *Calculations*

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

6.1 Nomenclature.

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

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

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

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

T_m = Average dry gas meter absolute temperature, °K (°R).

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

V_a = Volume of sample aliquot titrated, ml.

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

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

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

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

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide.

6.2 Dry sample gas volume, corrected to standard conditions.

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

Equation 6-1

where:

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

6.3 Sulfur dioxide concentration.

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

Equation 6-2

where:

K_2 = 32.03 mg/meq. for metric units.
= 7.061×10⁻⁵ lb/meq. for English units.

7. *Bibliography*

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

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

3. Matty, R. E. and E. K. Diehl. Measuring Flue-Gas SO_2 and SO_3. Power. 101: 94-97. November 1957.

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

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

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

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

8. Knoll, J. E. and M. R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. Environmental Protection Agency. Research Triangle Park, N.C. EPA-600/4-76-038. July 1976.

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

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

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

2. *Apparatus*

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

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

---

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

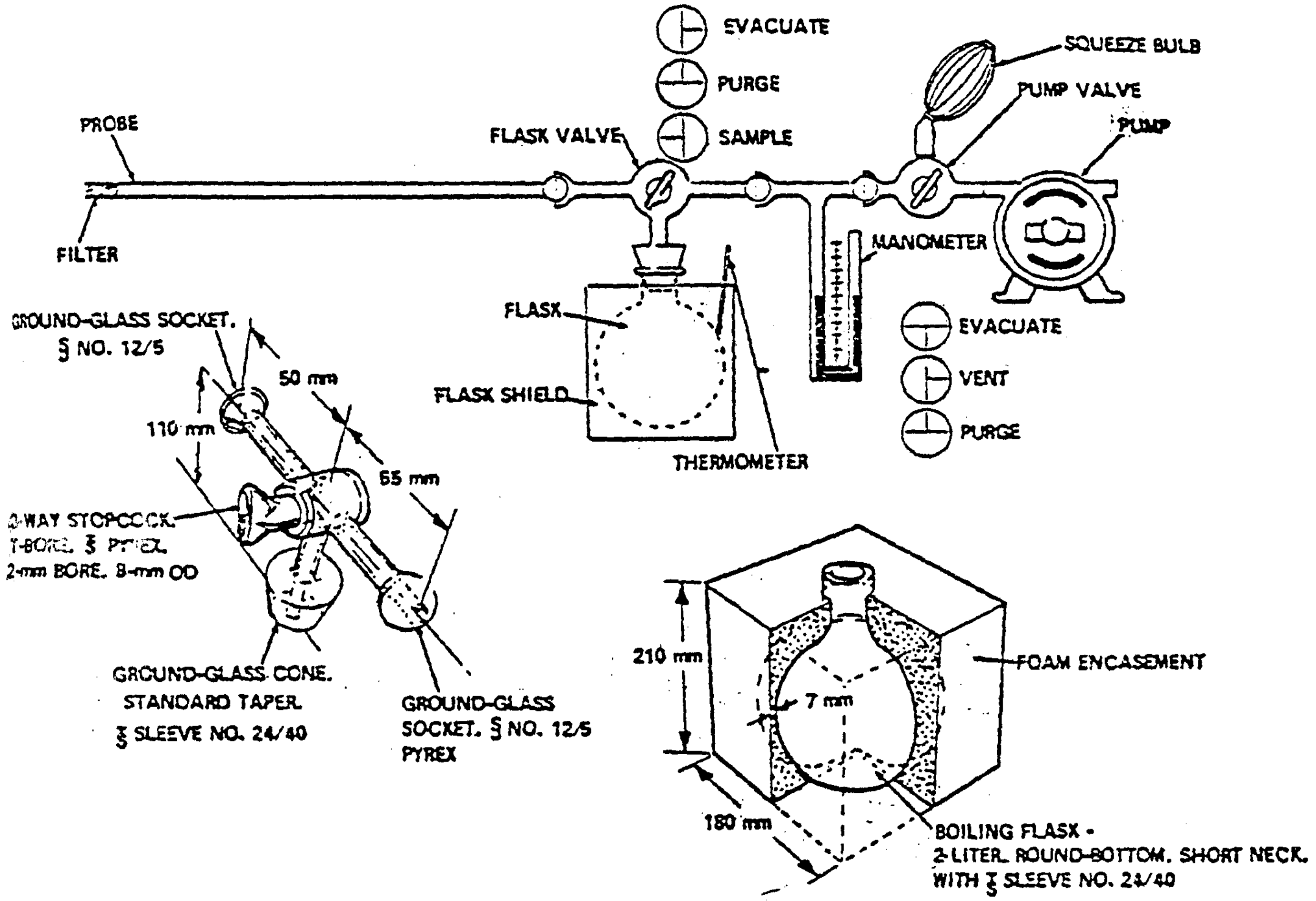


Figure 7-1. Sampling train, flask valve, and flask.

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

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

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

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

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

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

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

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

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

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

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

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

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

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

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

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

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

2.3.4 Dropping Pipette or Dropper. Three required.

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

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

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

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

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

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

2.3.11 Analytical Balance. To measure to within 0.1 mg.

3. Reagents

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

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

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

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

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

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

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

3.3.2 Phenol. White solid.

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

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

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

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

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

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

4. Procedures

4.1 Sampling.

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

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

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

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

5. Calibration

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

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination. For both fixed and variable wavelength spectrophotometers, calibrate against standard certified wavelength of 410 nm, every 6 months. Alternatively, for variable wave length spectrophotometers, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution (see Section 5.2.2). If a peak does not occur, the spectrophotometer is probably malfunctioning, and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance for both the standards and samples.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of the KNO_3 working standard solution (1 ml=100 μg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1N), dropwise, until the pH is between 9 and 12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

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

Equation 7-1

where:

K_c = Calibration factor

A_1 = Absorbance of the 100-μg NO_2 standard

A_2 = Absorbance of the 200-μg NO_2 standard

A_3 = Absorbance of the 300-μg NO_2 standard

A_4 = Absorbance of the 400-μg NO_2 standard

5.3 Barometer. Calibrate against a mercury barometer.

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

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

5.6 Analytical Balance. Calibrate against standard weights.

6. Calculations

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

6.1 Nomenclature.

A = Absorbance of sample.

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

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

K_c = Spectrophotometer calibration factor.

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

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

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

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

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

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

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

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

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

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

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

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

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

Equation 7-2

where:

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

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

6.3 Total μg NO_2 per sample.

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

Equation 7-3

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

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

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

Equation 7-4

where:

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

$$= 6.243\times10^{-5}\,\frac{\text{lb/scf}}{\mu\text{g/ml}}\text{ for English units}$$

7. Bibliography

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, p. 329-330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, Pa. 1968. ASTM Designation D-1608-60, p. 725-729.

3. Jacob, M. B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, p. 351-356.

4. Beatty, R. L., L. B. Berger, and H. H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R. I. 3687. February 1943.

5. Hamil, H. F. and D. E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. October 5, 1973.

6. Hamil, H. F. and R. E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. May 8, 1974.

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

1. Principle and Applicability

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

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter (0.03×10^{-7} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m³ (0.74×10^{-7} lb/ft³) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (35.3 ft³) gas sample is about 12,500 mg/m³ (7.7×10^{-4} lb/ft³). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

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

Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the Administrator); however, the procedure used for particulate matter must be consistent with the specifications and procedures given in Method 5.

2. Apparatus

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

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

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

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

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

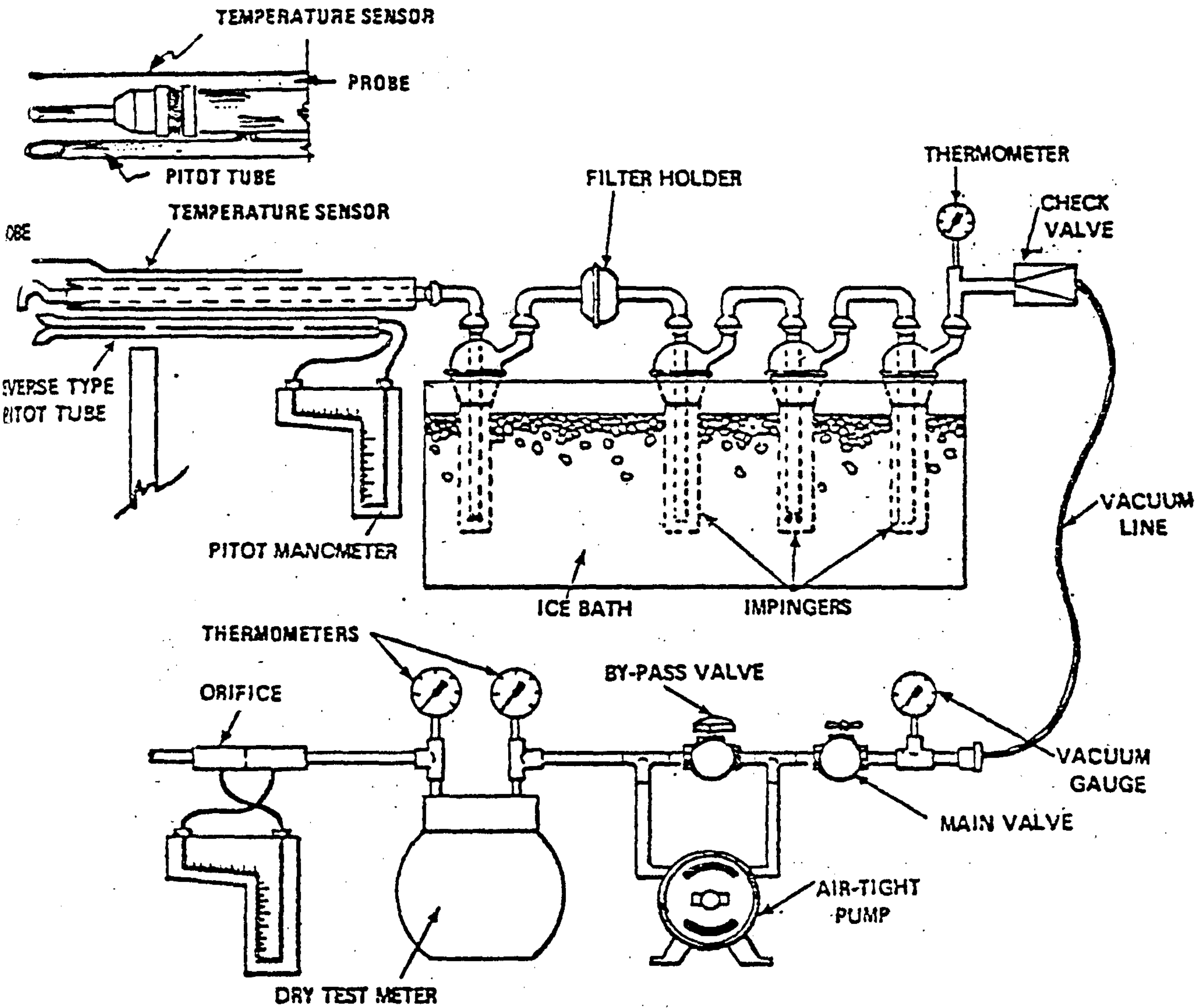


Figure 8-1: Sulfuric acid mist sampling train.

.4 Differential Pressure Gauge. Same as Method 5, ion 2.1.4.

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

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

.7 Metering System. Same as Method 5, Section 1.

.8 Barometer. Same as Method 5, Section 2.1.9.

.9 Gas Density Determination Equipment. Same Method 5, Section 2.1.10.

.10 Temperature Gauge. Thermometer, or equivato measure the temperature of the gas leaving the nger train to within 1° C (2° F).

Sample Recovery.

.1 Wash Bottles. Polyethylene or glass, 500 ml.

.2 Graduated Cylinders. 250 ml, 1 liter. (Volumetric flasks may also be used.)

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

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

2.3 Analysis.

2.3.1 Pipettes. Volumetric 25 ml, 100 ml.

2.3.2 Burrette. 50 ml.

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

2.3.4 Graduated Cylinder. 100 ml.

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

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

3. *Reagents*

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

3.1 Sampling.

3.1.1 Filters. Same as Method 5, Section 3.1.1.

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

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

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

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

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

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water. Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

3.3 Analysis.

3.3.1 Water. Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

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

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

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

4. *Procedure*

4.1 Sampling.

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

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

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

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

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

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

PLANT ____________

LOCATION ____________

OPERATOR ____________

DATE ____________

RUN NO. ____________

SAMPLE BOX NO. ____________

METER BOX NO. ____________

METER ΔH@ ____________

C FACTOR ____________

PITOT TUBE COEFFICIENT, Cp ____________

SCHEMATIC OF STACK CROSS SECTION

STATIC PRESSURE, mm Hg (in. Hg) ____________

AMBIENT TEMPERATURE ____________

BAROMETRIC PRESSURE ____________

ASSUMED MOISTURE, % ____________

PROBE LENGTH, m (ft) ____________

NOZZLE IDENTIFICATION NO. ____________

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ____________

PROBE HEATER SETTING ____________

LEAK RATE, m³/min, (cfm) ____________

PROBE LINER MATERIAL ____________

FILTER NO. ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S), °C (°F)	VELOCITY HEAD (ΔP_S), mm H_2O (in. H_2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H_2O (in. H_2O)	GAS SAMPLE VOLUME, m³ (ft³)	GAS SAMPLE TEMPERATURE AT DRY GAS METER: INLET, °C (°F)	GAS SAMPLE TEMPERATURE AT DRY GAS METER: OUTLET, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 8-2. Field data.

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

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

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

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

4.2 Sample Recovery.

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

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

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

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

4.3 Analysis.

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

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

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

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

5. *Calibration*

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

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

6. *Calculations*

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

6.1 Nomenclature.

- A_n = Cross-sectional area of nozzle, m² (ft²).
- B_{ws} = Water vapor in the gas stream, proportion by volume.
- $C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).
- C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).
- I = Percent of isokinetic sampling.
- N = Normality of barium perchlorate titrant, g equivalents/liter.
- P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
- P_s = Absolute stack gas pressure, mm Hg (in. Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- T_m = Average absolute dry gas meter temperature (see Figure 8–2), ° K (° R).
- T_s = Average absolute stack gas temperature (see Figure 8–2), ° K (° R).
- T_{std} = Standard absolute temperature, 293° K (528° R).
- V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.
- V_{lc} = Total volume of liquid collected in impingers and silica gel, ml.
- V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
- $V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).
- v_s = Average stack gas velocity, calculated by Method 2, Equation 2–9, using data obtained from Method 8, m/sec (ft/sec).
- V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.
- V_t = Volume of barium perchlorate titrant used for the sample, ml.
- V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
- Y = Dry gas meter calibration factor.
- ΔH = Average pressure drop across orifice meter, mm (in.) H_2O.
- θ = Total sampling time, min.
- 13.6 = Specific gravity of mercury.
- 60 = sec/min.
- 100 = Conversion to percent.

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

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

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

Equation 8–1

where:

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

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

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

6.5 Sulfuric acid mist (including SO_3) concentration.

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

Equation 8–2

where:

K_2 = 0.04904 g/milliequivalent for metric units.
= 1.081×10^{-4} lb/meq for English units.

6.6 Sulfur dioxide concentration.

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

Equation 8–3

where:

K_3 = 0.03203 g/meq for metric units.
= 7.061×10^{-4} lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

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

Equation 8–4

where:

K_4 = 0.003464 mm Hg-m³/ml-°K for metric units.
= 0.002678 in. Hg-ft³/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std}\, 100}{T_{std}\, v_s\, \theta\, A_n P_s\, 60\, (1 - B_{ws})} = K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Equation 8–5

where:

K_5 = 4.320 for metric units.
= 0.09450 for English units.

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

7. *Bibliography*

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

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

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

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

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

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

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

* * * * *

(Secs. 111, 114, 301(a), Clean Air Act, sec. 4(a) of Pub. L. 91–604, 84 Stat. 1683; sec. 4(a) of Pub. L. 91–604, 84 Stat. 1687; sec. 2 of Pub. L. 90–148, 81 Stat. 504 [42 U.S.C. 1857c–6, 1857c–9, 1857g(a)].)

[FR Doc.77-13608 Filed 8-17-77;8:45 am]

Attachment G

Determination of Particulate Emissions from Stationary Sources

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 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

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

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

3.3.1 Nomenclature.

B_{wm} = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.

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

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

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.

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

R = Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³)/lb-mole) (°R) for English units.

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

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

V_f = Final volume of impinger contents, ml.

V_i = Initial volume of impinger contents, ml.

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

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

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

3.3.2 Volume of water vapor collected.

$$V_{wc} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w} = K_1 (V_f - V_i)$$

Equation 4-5

where:
K_1 = 0.001333 m³/ml for metric units
= 0.04707 ft³/ml for English units.

3.3.3 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right) = K_2 \frac{V_m P_m}{T_m}$$

Equation 4-6

where:
K_2 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

3.3.4 Approximate moisture content.

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

Equation 4-7

4. *Calibration*

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

5. *Bibliography*

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, N.C. Publication No. AP-40. 1973.

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

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

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

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

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

2. *Apparatus*

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Section 7); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

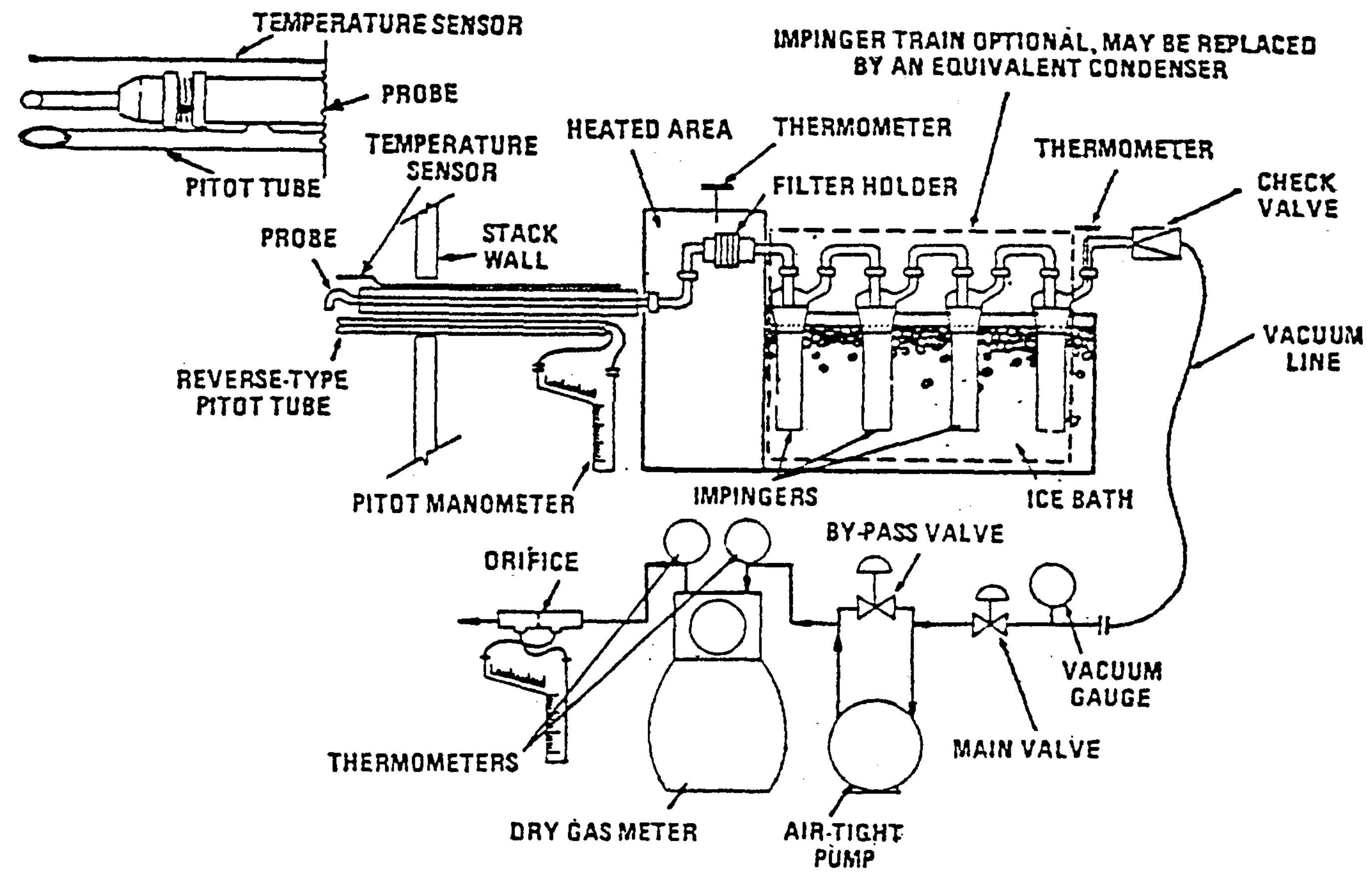


Figure 5 1. Particulate-sampling train.

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

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

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

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

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[2] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

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

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

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

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

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

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample 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.

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

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

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

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is

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

the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

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

2.2 Sample Recovery. The following items are needed.

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

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

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

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

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

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

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

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

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

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

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

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

3. *Reagents*

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

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (≤0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

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

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

3.1.4 Crushed Ice.

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

3.2 Sample Recovery. Acetone—reagent grade, ≤0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

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

4. *Procedure*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

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

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

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

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.

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

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

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

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

PLANT ____________

LOCATION ____________

OPERATOR ____________

DATE ____________

RUN NO. ____________

SAMPLE BOX NO. ____________

METER BOX NO. ____________

METER ΔH@ ____________

C FACTOR ____________

PITOT TUBE COEFFICIENT, C_p ____________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE ____________

BAROMETRIC PRESSURE ____________

ASSUMED MOISTURE, % ____________

PROBE LENGTH, m (ft) ____________

NOZZLE IDENTIFICATION NO. ____________

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ____________

PROBE HEATER SETTING ____________

LEAK RATE, m^3/min. (cfm) ____________

PROBE LINER MATERIAL ____________

STATIC PRESSURE, mm Hg (in. Hg) ____________

FILTER NO. ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S), mm (in.) H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER INLET °C (°F)	GAS SAMPLE TEMPERATURE AT DRY GAS METER OUTLET °C (°F)	FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

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

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

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Plant ____________________

Date ____________________

Run No. ____________________

Filter No. ____________________

Amount liquid lost during transport ____________________

Acetone blank volume, ml ____________________

Acetone wash volume, ml ____________________

Acetone blank concentration, mg/mg (equation 5-4) ____________________

Acetone wash blank, mg (equation 5-5) ____________________

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
	Less acetone blank		
	Weight of particulate matter		

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

* CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml):

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

Figure 5-3. Analytical data.

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

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

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

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

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

5. *Calibration*

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

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

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD–0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD–0576.

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

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

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD–0576. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used.

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

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. *Calculations*

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

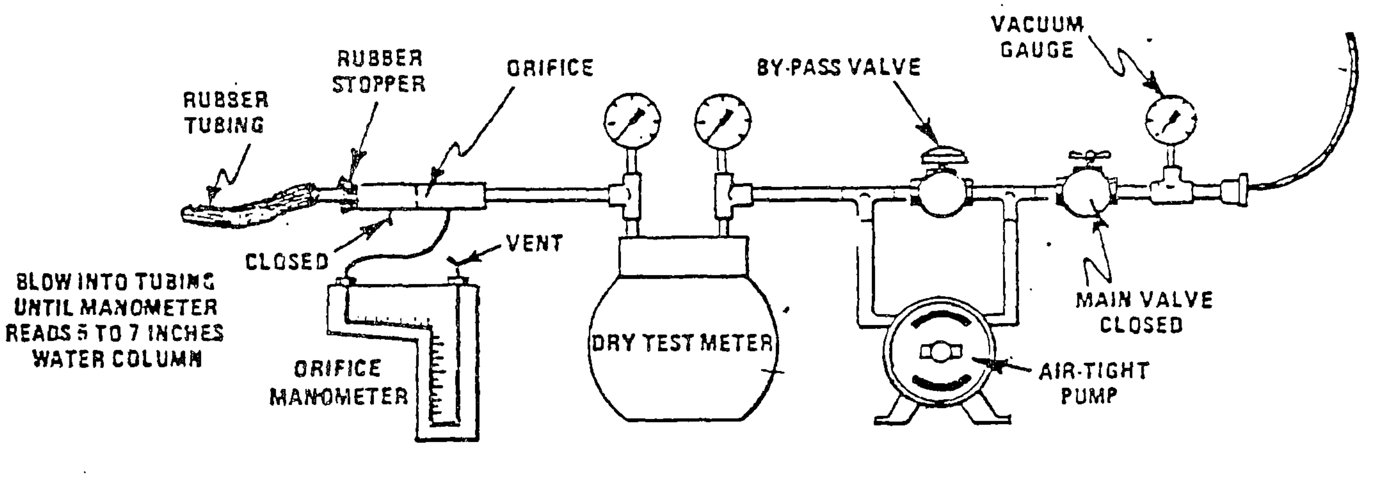


Figure 5-4. Leak check of meter box.

6.1 Nomenclature

A_n = Cross-sectional area of nozzle, m² (ft²).

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

C_a = Acetone blank residue concentrations, mg/g.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i=1, 2, 3 . . . . n), m³/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m³/min (cfm).

m_n = Total amount of particulate matter collected, mg.

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

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

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

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

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

R = Ideal gas constant, 0.06236 mm Hg-m³/°K-g-mole (21.85 in. Hg-ft³/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R).

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

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

V_a = Volume of acetone blank, ml.

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

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

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

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

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

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

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

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

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

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

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

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

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

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

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

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

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

Equation 5-1

where:

m_1 = 0.3868 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

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

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

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

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

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

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

6.4 Volume of water vapor.

Equation 5-2

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

where:

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

6.5 Moisture Content.

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

Equation 5-3

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

6.6 Acetone Blank Concentration.

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

Equation 5-4

6.7 Acetone Wash Blank.

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

Equation 5-5

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

6.9 Particulate Concentration.

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

Equation 5-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m³	0.02832
g/ft³	gr/ft³	15.43
g/ft³	lb/ft³	2.205×10⁻³
g/ft³	g/m³	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I = \frac{100\ T_s[K_3 V_{1c} + (V_m/T_m)(P_{bar} + \Delta H/13.6)]}{60\ \theta v_s P_s A_n}$$

Equation 5-7

where:

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

6.11.2 Calculation From Intermediate Values.

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

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

Equation 5-8

where:

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

6.12 Acceptable Results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make judgments. Otherwise, reject the results and repeat the test.

7. *Bibliography*

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. Dec. 6, 1967.

2. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, N.C. APTD-0581. April, 1971.

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

4. Smith, W. S., R. T. Shigehara, and W. F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo. June 14-19, 1970.

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

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

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

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

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, Pa. 1974. pp. 617-622.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

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

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m³ (2.12×10⁻⁷ lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ of SO_2 can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m³.

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

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

2. *Apparatus*

Attachment E

Determination of Total Polychlorinated Biphenyl (PCB) Emissions from Industrial, Sewage Sludge, and Municipal Refuse Incinerators (Draft Method)

PART A. INDUSTRIAL, SEWAGE SLUDGE, AND MUNICIPAL REFUSE INCINERATORS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The total PCBs in the train are determined by perchlorination to decachlorobiphenyl (DCB) and gas chromatographic determination of the DCB.

1.2 Applicability. This method is applicable for the determination of PCB emissions (both vaporous and particulate) from industrial, sewage sludge, and municipal refuse incinerators.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. However, the sensitivity of the total method as described here is about 10 ng DCB for each analytical replicate.

3. Interferences

Excessive quantities of acid-resistant organics may cause significant interferences obscuring the analysis of DCB in the perchlorinated extracts. Biphenyl, although unlikely to be present in samples from combustion sources, can form DCB in the perchlorination processes.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Adhesives must not be used to hold TFE® liners on lids, and lubricating and sealing greases must not be used on any sample exposed portions of the sampling train.

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95%.

5. Apparatus

5.1 Sampling Train. See Figure A-1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train. Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle--Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30 degrees and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

5.1.2 Probe liner--Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases; such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Administrator. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube--Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge--Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However,

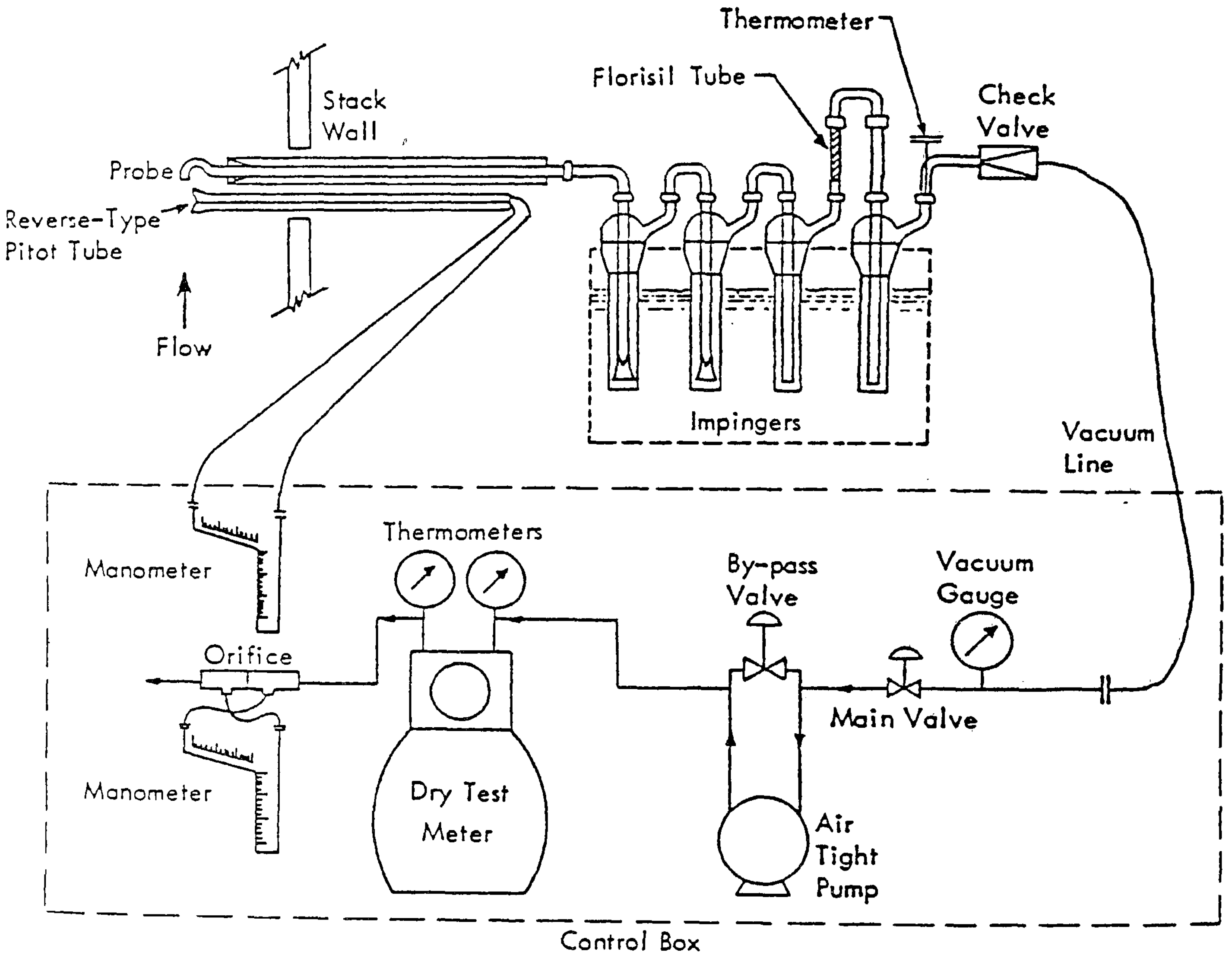


Figure A-1. PCB Sampling Train for Incinerators micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Administrator may be used when conditions warrant.

5.1.5 Impingers--Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure A-1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

5.1.6 Solid adsorbent tube--Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure A-2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system--Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer--Mercury, aneroid, or other barometers 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 weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Sample Recovery

5.2.1 Ground glass caps--To cap off adsorbent tube and the other sample exposed portions of the train.

5.2.2 Teflon FEP® wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.2.3 Sample storage containers--Glass bottles, 1 liter, with TFE®-lined screw caps.

5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.

5.2.5 Aluminum foil--Heavy duty.

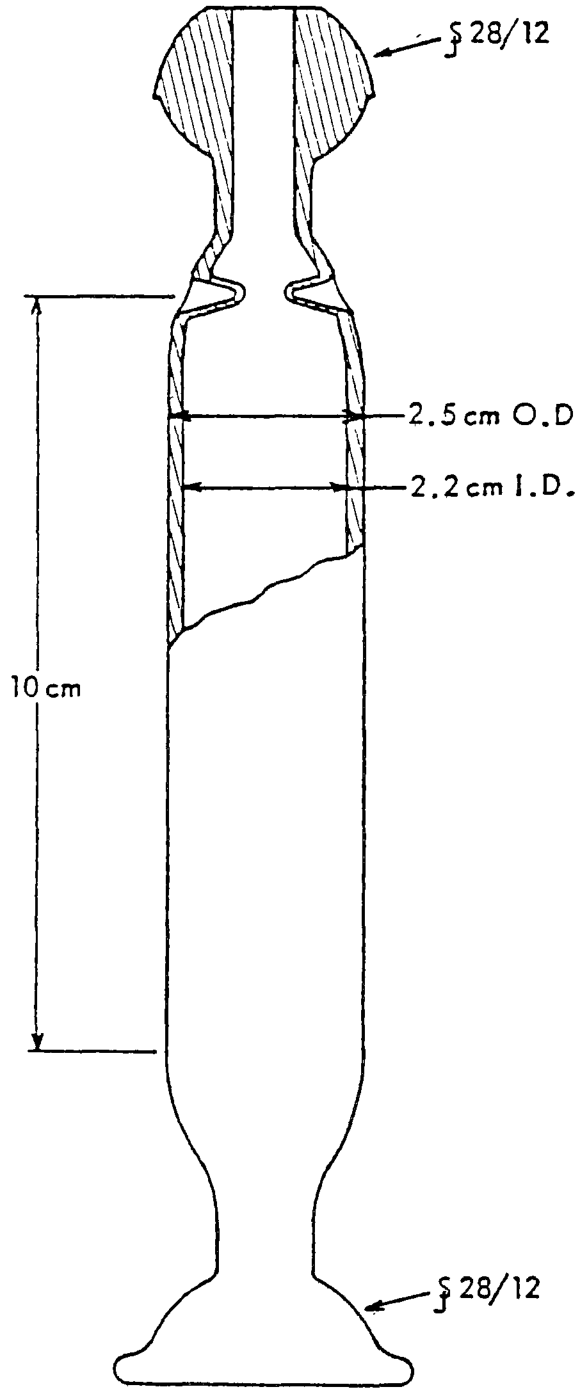


Figure A-2. Florisil Adsorbent Tube

5.2.6 Metal can--To recover used silica gel.

5.3 Analysis

5.3.1 Glass Soxhlet extractors--40 mm ID complete with 45/50 $\mathfrak{F}$ condenser, 24/40 $\mathfrak{F}$ 250 ml round bottom flask, heating mantle for 250 ml flask, and power transformer.

5.3.2 Teflon FEP wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.3.3 Separatory funnel--1,000 ml with TFE® stopcock.

5.3.4 Kuderna-Danish concentrators--500 ml.

5.3.5 Steam bath.

5.3.6 Separatory funnel--50 ml with TFE® stopcock.

5.3.7 Volumetric flask--25.0 ml, glass.

5.3.8 Volumetric flask--5.0 ml, glass.

5.3.9 Culture tubes--13 x 100 mm, glass with TFE®-lined screw caps.

5.3.10 Pipette--5.0 ml glass.

5.3.11 Aluminum block--Drilled to support culture tubes while heating.

5.3.12 Hot plate--Capable of heating to 200°C.

5.3.13 Teflon®-glass syringe--1 ml, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.3.14 Syringe--10 µl, Hamilton 701N or equivalent.

5.3.15 Gas chromatograph--Fitted with electron capture detector capable of operation at 300°C and with 2 mm ID x 1.8 mm glass column packed with 3% OV-210 on 100/120 mesh inert support (e.g., Supelcoport®).

5.3.16 Electric muffle furnace--Capable of heating to 650°C.

5.3.17 Electric oven--Capable of heating to 150°C.

5.3.18 Disposable glass pipettes with bulbs--To aid transfer of the extracts.

5.3.19 Porcelain casserole--Capable of withstanding temperatures as high as 650°C.

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Co., 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water--Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel--Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Sample Recovery

6.2.1 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3 Analysis

6.3.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.3 Water--Deionized and then glass-distilled, stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.3.4 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.3.5 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.3.6 Antimony pentachloride ($SbCl_5$)--Baker Analyzed Reagent or equivalent.

6.3.7 Hydrochloric acid (HCl) solution--ACS reagent grade or equivalent, 50% in water.

6.3.8 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.3.9 Decachlorobiphenyl--RFP Corp., No. RPC-60, or equivalent.

6.3.10 Compressed nitrogen--Prepurified.

6.3.11 Carborundum boiling stones--Hengar Co. No. 133-B or equivalent, rinsed with hexane.

7. Procedure

Caution: Section 7.1.1 should be done in the laboratory.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularily contamination problems.

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

7.1.1.1 Cleaning glassware. All glass parts of the train upstream of and including the adsorbent tube, 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." 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.

7.1.1.2 Solid adsorbent tube. Weigh 7.5 g of Florisil, activated within the last 30 days and still warm from storage in a 110°C oven, into the adsorbent tube (pre-rinsed with hexane) with a glass wool plug in the downstream end. Place a second glass wool plug in the tube to hold the sorbent in the tube. Cap both ends of the tube with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Determine the molecular weight of the stack gases using Method 3.

Select a nozzle size based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. 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.

Select a suitable probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a sampling time appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

It is recommended that a buzzer-timer be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

In some circumstances, e.g., short batch processes, it may be necessary to sample through two or more batches to obtain sufficient sample volume. In these cases, sampling should cease during loading/unloading of the furnace.

7.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, rinse all parts of the train upstream of the adsorbent tube with hexane.

Mark the probe with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

Place 200 ml of water in each of the first two impingers, and leave the third impinger empty. CAUTION: do not use sealant greases in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 10.1. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

Assemble the train as shown in Figure A-1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Place crushed ice around the impingers.

7.1.4 Leak check procedure--After the sampling train has been assembled, turn on and set (if applicable) the probe heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of bypass valve. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) 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 and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Train operation--During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained. During the run, do not change the nozzle or any other part of the train in front of and including the Florisil tube.

For each run, record the data required on the data sheets. An example is shown in Figure A-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Be sure to level and zero the manometer.

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

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

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

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator. To minimize chance of extracting deposited material, be careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

FIELD DATA

PLANT ____________________
DATE ____________________
SAMPLING LOCATION ____________________
SAMPLE TYPE ____________________
RUN NUMBER ____________________
OPERATOR ____________________
AMBIENT TEMPERATURE ____________________
BAROMETRIC PRESSURE ____________________
STATIC PRESSURE, (P_s) ____________________
FILTER NUMBER (s) ____________________

PROBE LENGTH AND TYPE ____________________
NOZZLE I.D. ____________________
ASSUMED MOISTURE, % ____________________
SAMPLE BOX NUMBER ____________________
METER BOX NUMBER ____________________
METER $\Delta H_{@}$ ____________________
C FACTOR ____________________
PROBE HEATER SETTING ____________________
HEATER BOX SETTING ____________________
REFERENCE Δp ____________________

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY ________ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			

COMMENTS

Figure A-3. Field Data Sheet

EPA (Dur) 235
4/72

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during a test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.* Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

7.1.6 Blank train--For each series of test runs, set up a blank train in a manner identical to that described above, but with the nozzle capped with aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Section 7.2.

7.2 Sample recovery. 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. Cap off the inlet to the train with a ground glass cap.

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

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

7.2.1 Adsorbent tube--Remove the Florisil tube from the train and cap it off with ground glass caps.

* With acceptability of the test run to be based on the same criterion as in 7.1.4

7.2.2 Sample container No. 1--Remove the first three impingers. Wipe off the outside of each impinger to remove excessive water and other debris, weigh (stem included), and record the weight on data sheet. Pour the contents directly into container No. 1 and seal.

7.2.3 Sample container No. 2--Rinse each of the first three impingers sequentially first with 30 ml acetone and then with 30 ml hexane, and put the rinses into container No. 2. Quantitatively recover material deposited in the probe using 100 ml acetone and then 100 ml hexane and add these rinses to container No. 2 and seal.

7.2.4 Silica gel container--Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Transfer the contents to the used silica gel can.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with 5 ml acetone and then with 15 ml hexane and put these rinses into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml on a steam bath and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50-ml separatory funnel and set the funnel aside.

7.3.1.2 Sample container No. 1. Transfer the aqueous sample to a 1,000-ml separatory funnel. Rinse the container with 20 ml acetone and then with two 20-ml portions of hexane, adding the rinses to the separatory funnel.

Extract the sample with three 100 ml portions of hexane, transferring the sequential extracts to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil extract. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

7.3.1.3 Sample container No. 2. Transfer the organic solution into a 1,000 ml separatory funnel. Rinse the container with two 20 ml portions of hexane and add the rinses to the separatory funnel. Wash the sample with three 100 ml portions of water. Discard the aqueous layer and transfer the organic layer to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil and impinger extracts.

7.3.2 Extract cleanup--Clean the combined extracts (in 50 ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples" Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25 ml volumetric flask and dilute to volume with hexane. Pipette three 5.0 ml aliquots into culture tubes for perchlorination. Retain the remaining 10 ml for later verification, if required (see Section 10.2).

7.3.3 Extract perchlorination--Evaporate the aliquots in the culture tubes just to dryness with a gentle stream of dry nitrogen. If the aliquots will not evaporate to dryness, refer to Section 10.3 concerning special cases. Add 0.2 ml antimony pentachloride with a 1 ml glass-TFE® syringe and seal the tube with a TFE®-lined screw cap. Heat the reaction mixture to 160°C for 2 hr by placing the tube in a hole in an aluminum block on a hot plate.

Allow the tube to cool to ambient room temperature before adding about 2 ml of 50% HCl in water to destroy residual antimony pentachloride. This is a convenient "stopping point" in the perchlorination procedure.

Extract the reaction mixture by adding about 1 ml hexane to the tube, shake, and allow layers to separate. Remove the upper hexane layer with a disposable pipette and filter through a micro column of anhydrous sodium sulfate directly into a 5 ml volumetric flask. Repeat the extraction three times for a total of four extractions. Dilute the extract to volume with hexane.

7.3.4 PCB determination--Assay the perchlorinated extracts for decachlorobiphenyl (DCB) by gas chromatographic comparison with DCB standard solutions and correct this result for the DCB concentration determined for the blank train. (Column temperature and carrier gas flow parameters of 240°C and 30 ml/min, are typically appropriate. The concentrations of the standard solutions should allow fairly close comparison with DCB in the sample extracts. Standards near 25 to 50 picograms/microliter may be appropriate.)

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than $\pm$ 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration--The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the DCB standard.

9. Calculations

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

9.1 Nomenclature

G_n = Corrected weight of DCB in nth perchlorinated aliquot (n = 1, 2, 3), µg.

G_s = Total weight of PCBs (as DCB) in sample, µg.

C_s = Concentration of PCBs in stack gas, µg/m^3, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

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

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

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 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/°K-g-mole (21.83 in. Hg-ft^3/° R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

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

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml. volume of water collected equals the weight increase in grams times 1 ml/gram

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

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

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

V_t = Total volume of sample, ml.

V_s = Stack gas velocity, calculated by EPA Method 2, m/sec (ft/sec).

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

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total Sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure A-3).

9.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [20° C, 760 mm Hg (68° F, 29.92 in. Hg)] by using Equation A-1).

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

Equation A-1

where $K = 0.3855\ ^{\circ}K/mm\ Hg$ for metric units

$= 17.65\ ^{\circ}R/in.\ Hg$ for English units

9.4 Volume of water vapor

$$V_{w(std)} = V_{1c} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K\, V_{1c}$$

Equation A-2

where $K = 0.00134\ m^3/ml$ for metric units

$= 0.0472\ ft^3/ml$ for English units

9.5 Moisture content

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

Equation A-3

If the liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

9.6 Concentration

9.6.1 Calculate the total PCB residue (as DCB) in the sample from the weights of DCB in the perchlorinated aliquots according to Equation A-4.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3} \qquad \text{Equation A-4}$$

9.6.2 Concentration of PCBs (as DCB) in stack gas. Determine the concentration of PCBs in the stack gas according to Equation A-5.

$$C_s = K \frac{G_s}{V_{m(std)}} \qquad \text{Equation A-5}$$

where $K = 35.31\ ft^3/m^3$

9.7 Isokinetic variation

9.7.1 Calculations from raw data.

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

Equation A-6

where $K = 0.00346$ mm Hg-m^3/ml-°K for metric units

$= 0.00267$ in. Hg-ft^3/ml-°R for English units

9.7.2 Calculations from intermediate values.

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

$$= K \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})} \qquad \text{Equation A-7}$$

where $K = 4.323$ for metric units

$= 0.0944$ for English units

9.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If 90% < I < 110%, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results.

10. Special Cases

10.1 Sampling moisture saturated or supersaturated stack gases. One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

10.2 PCB verification. It is recommended that an unperchlorinated aliquot from at least one sample be subjected to GC/MS examination to verify that PCB isomers are present.

To accomplish this, the unperchlorinated portion of each extract is first screened by GC with the same chromatographic system used for DCB determination except for a cooler column temperature, typically 165 to 200°C. The elution patterns are compared with those of commercial PCB mixtures (in hexane solution) to determine the most similar mixture.

After determining what PCB isomers are possible present, the sample is examined by GC/MS using multiple ion selection techniques for ions characteristic of the molecular clusters of the PCBs possibly present.

10.3 Evaporation of extracts for perchlorination. For cases where the extract will not evaporate to dryness or excessive PCB loss by volatilization is suspected, the hexane may be removed by azeotrophic evaporation from the hexane/chloroform mixture.

Add 3 ml of chloroform to the aliquot in the culture tube. Add a boiling chip and concentrate by slow boiling in a water bath to 1 ml. Repeat the chloroform addition and evaporation three times in order to remove all residual hexane. Then further concentrate (slowly) to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C or the solvent be evaporated to dryness. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of solvent level with another reaction vial containing 0.1 ml of chloroform. When a volume of 0.1 ml is achieved, cap the reaction vial immediately and allow to cool. Proceed with the perchlorination as described in Section 7.3.3.

11. References

Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

1973 Annual Book of ASTM Standards, Part 23, Designation: D 1179-72.

Thompson, J. F., Ed., "Analysis of Pesticide Residues in Human and Environmental Samples," Environmental Protection Agency, Research Triangle Park, N.C., 1974.

Attachment F

Determination of Nitrogen Oxide Emissions from Stationary Sources

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

4. Procedure.

4.1 Sampling.

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

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

With the probe disconnected, place a vacuum gauge at the inlet to the bubbler and pull a vacuum of 250 mm (10 in.) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end to prevent back flow of the impinger fluid.

Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency. The procedure used in Method 5 is not suitable for diaphragm pumps.

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

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

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

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

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

(NOTE.—Protect the 0.0100 N barium perchlorate solution from evaporation at all times.)

5. Calibration

5.1 Metering System.

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

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

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

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

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

5.4 Barometer. Calibrate against a mercury barometer.

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

6. Calculations

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

6.1 Nomenclature.

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

6.2 Dry sample gas volume, corrected to standard conditions.

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

Equation 6-1

where:

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

6.3 Sulfur dioxide concentration.

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

Equation 6-2

where:

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

7. Bibliography

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

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

3. Matty, R. E. and E. K. Diehl. Measuring Flue-Gas SO_2 and SO_3. Power. *101*: 94-97. November 1957.

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

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

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

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

8. Knoll, J. E. and M. R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. Environmental Protection Agency. Research Triangle Park, N.C. EPA-600/4-76-038. July 1976.

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

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

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

2. Apparatus

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

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

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

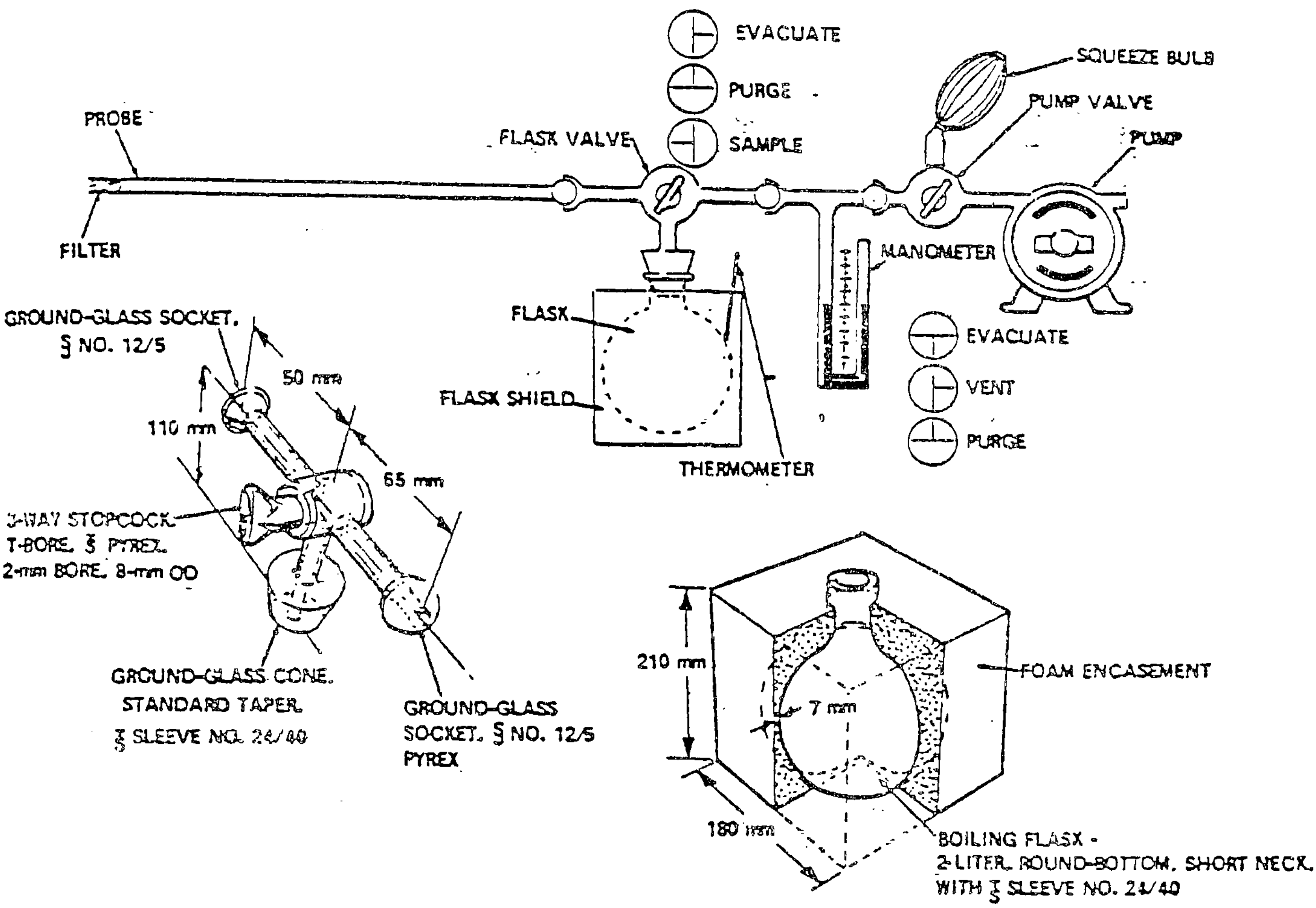


Figure 7-1. Sampling train, flask valve, and flask.

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

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

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

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

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

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

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

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

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

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

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

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

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

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

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

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

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

2.3.4 Dropping Pipette or Dropper. Three required.

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

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

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

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

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

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

2.3.11 Analytical Balance. To measure to within 0.1 mg.

3. *Reagents*

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

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

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

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

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

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

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

3.3.2 Phenol. White solid.

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

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

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

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

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

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

4. *Procedures*

4.1 Sampling.

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

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

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

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

5. *Calibration*

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

5.2 Spectrophotometer Calibration

5.2.1 Optimum Wavelength Determination. For both fixed and variable wavelength spectrophotometers, calibrate against standard certified wavelength of 410 nm, every 6 months. Alternatively, for variable wave length spectrophotometers, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution (see Section 5.2.2). If a peak does not occur, the spectrophotometer is probably malfunctioning, and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance for both the standards and samples.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of the KNO_3 working standard solution (1 ml = 100 μg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1N), dropwise, until the pH is between 9 and 12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

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

Equation 7–1

where:

K_c = Calibration factor

A_1 = Absorbance of the 100-μg NO_2 standard

A_2 = Absorbance of the 200-μg NO_2 standard

A_3 = Absorbance of the 300-μg NO_2 standard

A_4 = Absorbance of the 400-μg NO_2 standard

5.3 Barometer. Calibrate against a mercury barometer.

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

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

5.6 Analytical Balance. Calibrate against standard weights.

6. *Calculations*

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

6.1 Nomenclature.

A = Absorbance of sample.

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

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

K_c = Spectrophotometer calibration factor.

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

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

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

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

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

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

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

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

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

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

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

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

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

Equation 7–2

where:

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

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

6.3 Total μg NO_2 per sample.

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

Equation 7–3

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

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

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

Equation 7–4

where:

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

$$= 6.243\times10^{-5}\ \frac{\text{lb/scf}}{\mu\text{g/ml}}\ \text{for English units}$$

7. *Bibliography*

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, p. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, Pa. 1968. ASTM Designation D–1608–60, p. 725–729.

3. Jacob, M. B. The Chemical Analysis of Air Pollutants. New York. Interscience Publishers, Inc. 1960. Vol. 10, p. 351–356.

4. Beatty, R. L., L. B. Berger, and H. H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R. I. 3687. February 1943.

5. Hamil, H. F. and D. E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. October 5, 1973.

6. Hamil, H. F. and R. E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. May 8, 1974.

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

1. *Principle and Applicability*

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

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter (0.03×10^{-7} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m³ (0.74 10^{-7} lb/ft³) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (35.3 ft³) gas sample is about 12,500 mg/m³ (7.7×10^{-4} lb/ft³). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

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

Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the Administrator); however, the procedure used for particulate matter must be consistent with the specifications and procedures given in Method 5.

2. *Apparatus*

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

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

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

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

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

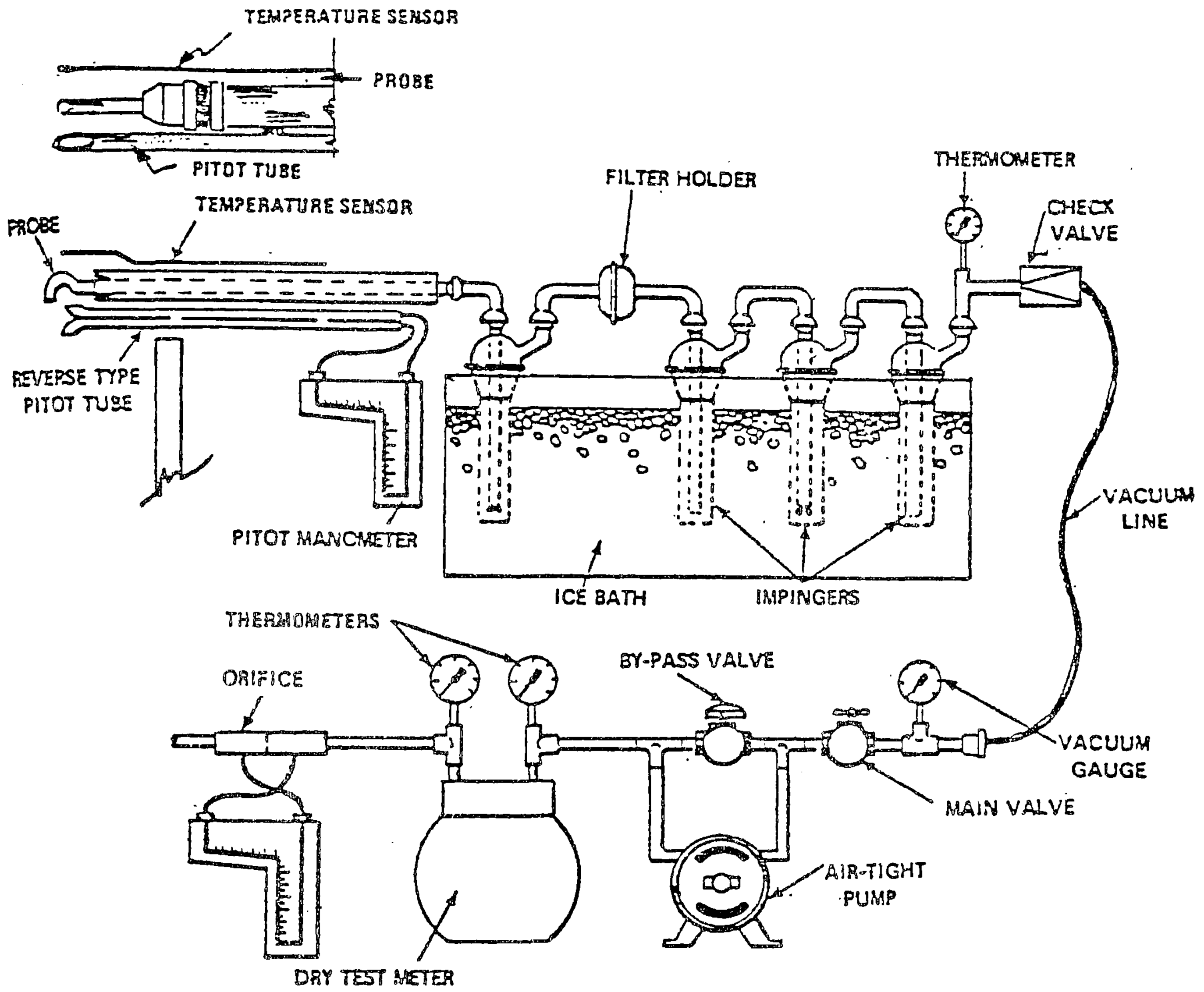


Figure 8-1: Sulfuric acid mist sampling train.

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

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

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

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

2.1.8 Barometer. Same as Method 5, Section 2.1.9.

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

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

2.2 Sample Recovery.

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

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

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

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

2.3 Analysis.

2.3.1 Pipettes. Volumetric 25 ml, 100 ml.

2.3.2 Burrette. 50 ml.

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

2.3.4 Graduated Cylinder. 100 ml.

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

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

3. *Reagents*

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

3.1 Sampling.

3.1.1 Filters. Same as Method 5, Section 3.1.1.

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

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

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

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

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

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water. Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

3.3 Analysis.

3.3.1 Water. Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

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

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

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

4. *Procedure*

4.1 Sampling.

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

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

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

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

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

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

PLANT ____________
LOCATION ____________
OPERATOR ____________
DATE ____________
RUN NO. ____________
SAMPLE BOX NO. ____________
METER BOX NO. ____________
METER ΔH@ ____________
C FACTOR ____________
PITOT TUBE COEFFICIENT, Cp ____________

SCHEMATIC OF STACK CROSS SECTION

STATIC PRESSURE, mm Hg (in. Hg) ____________
AMBIENT TEMPERATURE ____________
BAROMETRIC PRESSURE ____________
ASSUMED MOISTURE, % ____________
PROBE LENGTH, m (ft) ____________
NOZZLE IDENTIFICATION NO. ____________
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ____________
PROBE HEATER SETTING ____________
LEAK RATE, m³/min, (cfm) ____________
PROBE LINER MATERIAL ____________
FILTER NO. ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S), °C (°F)	VELOCITY HEAD (ΔP_S), mm H_2O (in. H_2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H_2O (in. H_2O)	GAS SAMPLE VOLUME, m³ (ft³)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET, °C (°F)	OUTLET, °C (°F)	
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 8-2. Field data.

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

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

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

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

4.2 Sample Recovery.

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

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

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

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

4.3 Analysis.

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

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

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

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

5. *Calibration*

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

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

6. *Calculations*

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

6.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m² (ft²).
B_{ws} = Water vapor in the gas stream, proportion by volume.
$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).
C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).
I = Percent of isokinetic sampling.
N = Normality of barium perchlorate titrant, g equivalents/liter.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_m = Average absolute dry gas meter temperature (see Figure 8-2), ° K (° R).
T_s = Average absolute stack gas temperature (see Figure 8-2), ° K (° R).
T_{std} = Standard absolute temperature, 293° K (528° R).
V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.
V_{lc} = Total volume of liquid collected in impingers and silica gel, ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).
v_s = Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 8, m/sec (ft/sec).
V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.
V_t = Volume of barium perchlorate titrant used for the sample, ml.
V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
Y = Dry gas meter calibration factor.
ΔH = Average pressure drop across orifice meter, mm (in.) H_2O.
θ = Total sampling time, min.
13.6 = Specific gravity of mercury.
60 = sec/min.
100 = Conversion to percent.

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

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

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

Equation 8-1

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

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

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

6.5 Sulfuric acid mist (including SO_3) concentration.

$$C_{H_2SO_4} = K_3 \frac{N(V_t - V_{tb}) \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 8-2

where:
K_3 = 0.04904 g/milliequivalent for metric units.
= 1.081×10⁻⁴ lb/meq for English units.

6.6 Sulfur dioxide concentration.

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

Equation 8-3

where:
K_3 = 0.03203 g/meq for metric units.
= 7.061×10⁻⁴ lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

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

Equation 8-4

where:
K_4 = 0.003464 mm Hg-m³/ml-°K for metric units.
= 0.002676 in. Hg-ft³/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std}\, 100}{T_{std}\, v_s\, \theta\, A_n P_s\, 60\, (1 - B_{ws})} = K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Equation 8-5

where:
K_5 = 4.320 for metric units.
= 0.09450 for English units.

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

7. *Bibliography*

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

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

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

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

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

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

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

• • • • •

(Secs. 111, 114, 301(a), Clean Air Act, sec. 4(a) of Pub. L. 91-604, 84 Stat. 1683; sec. 4(a) of Pub. L. 91-604, 84 Stat. 1687; sec. 2 of Pub. L. 90-148, 81 Stat. 504 [42 U.S.C. 1857c-6, 1857c-9, 1857g(a)].)

[FR Doc.77-13608 Filed 8-17-77;8:45 am]

Attachment G

Determination of Particulate Emissions from Stationary Sources

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 ft³) 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 4-3.

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

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

3.3.1 Nomenclature:

B_{wm} = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole)
P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³)/lb-mole) (°R) for English units.
T_m = Absolute temperature at meter, °K (°R)
T_{std} = Standard absolute temperature, 293° K (528° R)
V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.
V_m = Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).
ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

3.3.2 Volume of water vapor collected.

$$V_{wc} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w} = K_1 (V_f - V_i)$$

Equation 4-5

where:
K_1 = 0.001333 m³/ml for metric units
= 0.04707 ft³/ml for English units.

3.3.3 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right) = K_2 \frac{V_m P_m}{T_m}$$

Equation 4-6

where:
K_2 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

3.3.4 Approximate moisture content.

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

Equation 4-7

4. Calibration

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

5. Bibliography

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, N.C. Publication No. AP-40. 1973.

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

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

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

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

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

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Section 7); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

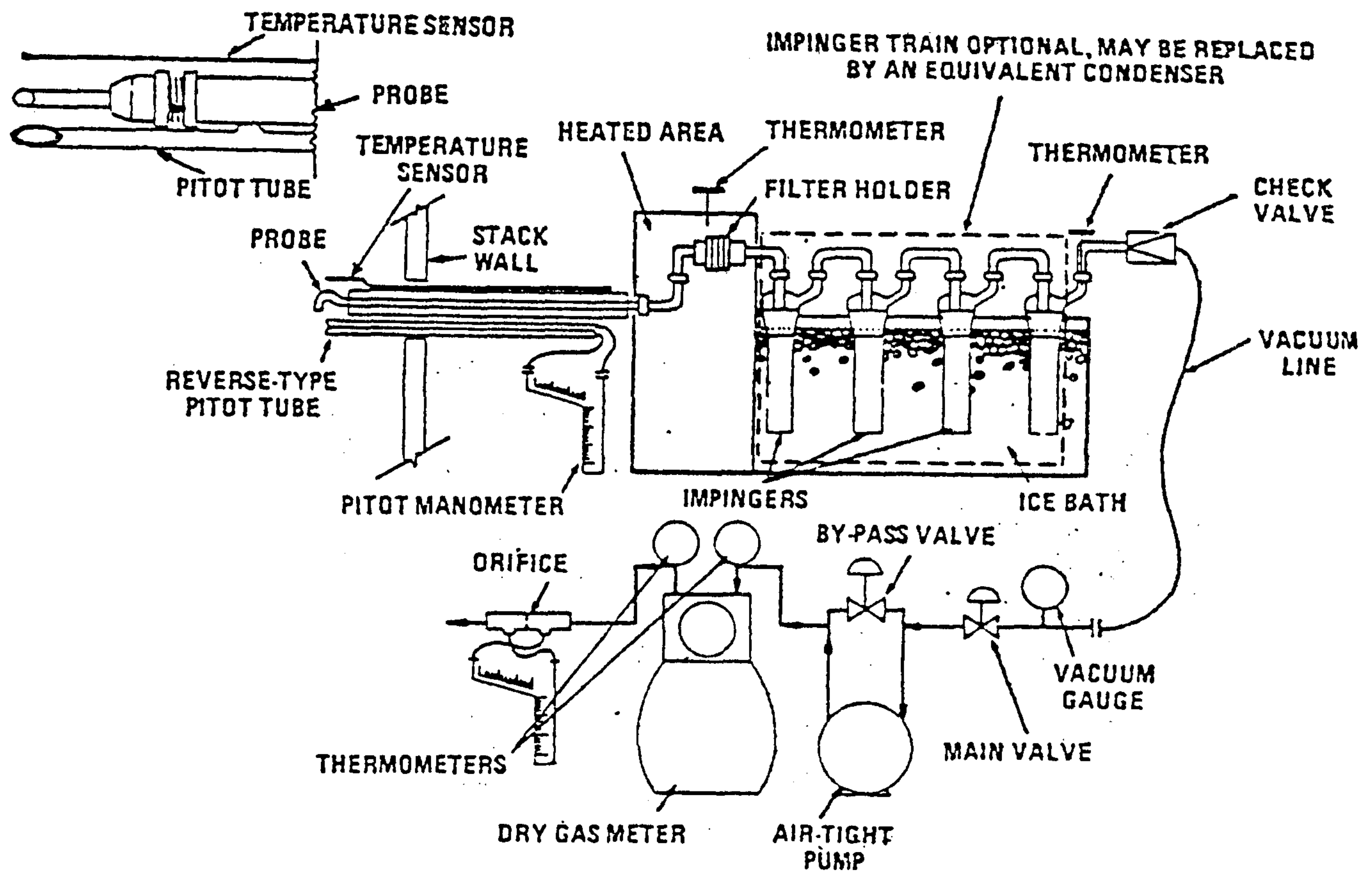


Figure 5-1. Particulate-sampling train.

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

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

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

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

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

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

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

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

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

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

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample 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.

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

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

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

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is

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

the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

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

2.2 Sample Recovery. The following items are needed.

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

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

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

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

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

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

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

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

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

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

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

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

3. Reagents

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

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (≤0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

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

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

3.1.4 Crushed Ice.

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

3.2 Sample Recovery. Acetone—reagent grade, ≤0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

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

4. Procedure

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

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

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

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

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

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

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

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

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

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

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

PLANT ____________

LOCATION ____________

OPERATOR ____________

DATE ____________

RUN NO. ____________

SAMPLE BOX NO. ____________

METER BOX NO. ____________

METER ΔH@ ____________

C FACTOR ____________

PITOT TUBE COEFFICIENT, C_p ____________

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE ____________

BAROMETRIC PRESSURE ____________

ASSUMED MOISTURE, % ____________

PROBE LENGTH, m (ft) ____________

NOZZLE IDENTIFICATION NO. ____________

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) ____________

PROBE HEATER SETTING ____________

LEAK RATE, m^3/min. (cfm) ____________

PROBE LINER MATERIAL ____________

STATIC PRESSURE, mm Hg (in. Hg) ____________

FILTER NO. ____________

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S), mm (in.) H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER: INLET °C (°F)	GAS SAMPLE TEMPERATURE AT DRY GAS METER: OUTLET °C (°F)	FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

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

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

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Plant ______________________________

Date ______________________________

Run No. ______________________________

Filter No. ______________________________

Amount liquid lost during transport ______________________________

Acetone blank volume, ml ______________________________

Acetone wash volume, ml ______________________________

Acetone blank concentration, mg/mg (equation 5-4) ______________________________

Acetone wash blank, mg (equation 5-5) ______________________________

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL	X	X	
		Less acetone blank	
		Weight of particulate matter	

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml.	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

* CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml):

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

Figure 5-3. Analytical data.

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

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

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

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

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

5. *Calibration*

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

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

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

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

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

5.4 Probe Heater Calibration. The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

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

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. *Calculations*

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

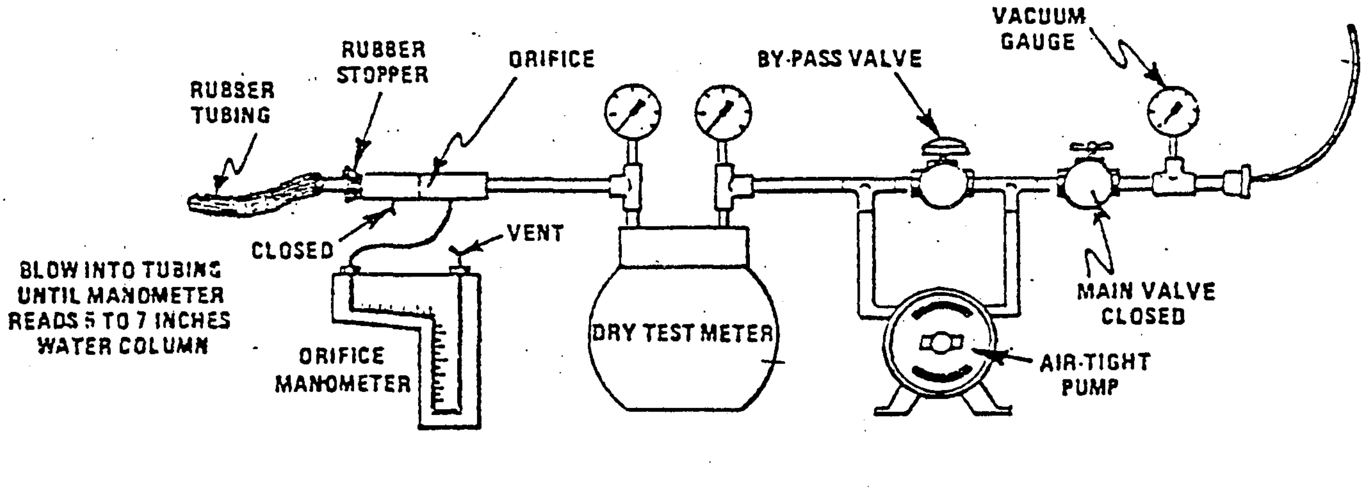


Figure 5-4. Leak check of meter box.

6.1 Nomenclature

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

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

C_a = Acetone blank residue concentrations, mg/g.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i = 1, 2, 3 . . . . n), m^3/min (cfm).

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

m_n = Total amount of particulate matter collected, mg.

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

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

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

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

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

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

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R).

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

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

V_a = Volume of acetone blank, ml.

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

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

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

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

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

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

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

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

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

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

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

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

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

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

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

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

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

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

Equation 5-1

where:
m_1 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

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

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

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

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

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

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

6.4 Volume of water vapor.

$$V_{w(std)}=V_{1c}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right)=K_2V_{1c}$$

Equation 5-2

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

6.5 Moisture Content.

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

Equation 5-3

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

6.6 Acetone Blank Concentration.

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

Equation 5-4

6.7 Acetone Wash Blank.

$$W_a=C_aV_{aw}\rho_a$$

Equation 5-5

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

6.9 Particulate Concentration.

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

Equation 5-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m³	0.02832
g/ft³	gr/ft³	15.43
g/ft³	lb/ft³	2.205×10⁻³
g/ft³	g/m³	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I=\frac{100\ T_s[K_3V_{1c}+(V_m/T_m)\ (P_{bar}+\Delta H/13.6)]}{60\ \theta v_s P_s A_n}$$

Equation 5-7

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

6.11.2 Calculation From Intermediate Values.

$$I=\frac{T_sV_{m(std)}P_{std}100}{T_{std}v_s\theta A_nP_s60(1-B_{ws})}$$

$$=K_4\frac{T_sV_{m(std)}}{P_sV_sA_n\theta(1-B_{ws})}$$

Equation 5-8

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

6.12 Acceptable Results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make judgments. Otherwise, reject the results and repeat the test.

7. *Bibliography*

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. Dec. 6, 1967.

2. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, N.C. APTD-0581. April, 1971.

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

4. Smith, W. S., R. T. Shigehara, and W. F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo. June 14-19, 1970.

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

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

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

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

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, Pa. 1974. pp. 617-622.

METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

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

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m³ (2.12×10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ of SO_2 can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m³.

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

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

2. *Apparatus*