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

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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.

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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 CO₂, and O₂ 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 modifications 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.

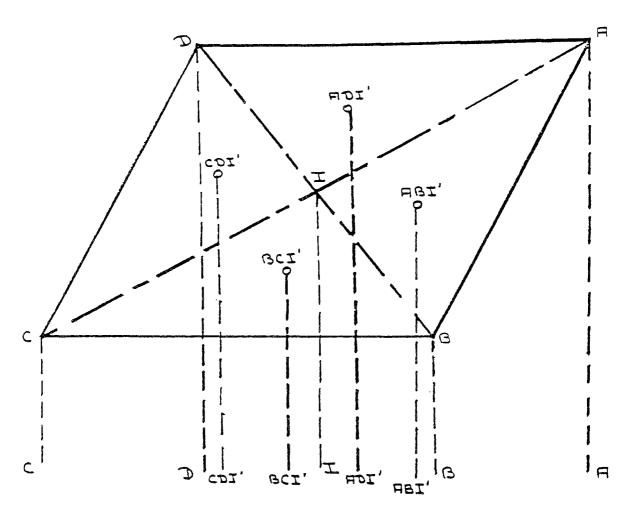
The plot should be defined by establishing transects along the suspected perimeter with sufficient surface samples taken to define the perimeter. Transects for subsurface samples should also be established that intersect through the approximate center of the suspected area with subsurface samples taken 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, 0.5 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 pcas. 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 ($\pm100^{\circ}\text{C}$) and 3 percent excess oxygen in the stack gas, or
- Maintenance of the introduced PCB wastes for a $1\frac{1}{2}$ -second dwell time at 1600° C ($\frac{+}{2}$ 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

1.S.A.	Positive	Negarire	i	C s .	ial te	C.F. 73	n Tr			ai. ne
t), be	element	j eleminati.		٠C.		ī -	٠Ł٠.		°C.	ř.
:	90 % Pt-10 % Rh	Place -	! 0	U	1450	3.2	te	2650	1700	3.00
P.	87 C. Pt-13 C. P.S.		: 0		1450					7:00
7	Chrome!-P	Alame.				- 300				
J, Y	Iroa	Con-	 — 2 00	to	750	- 300	io	14 0	1000	1800
Т	Copper	Stantan Con-	200	ಒ	350	-200	to	650	600	1100
	Chromel-P	S'antao Cor-	-100	to	1000	-150	to	1800	1000	1800
		5130130								

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

Table 2: Corrosion Characteristics of Common Thermocouples

Type of Thermoceuple standard vs. plantium-roodium	Influence of Temperature and Gas Atmospheres Resistance to oxidizing atmospheres rervey.com Resistance to reducing atmospheres room
Chromei-P vs. Alumei	N. Assinum corrodes easily above 1000°C. Should be used in maright ceramic protecting tube. Resistance to outding almosphere: good to very good. Resistance to reducing almosphere: poor.
Iron va. Constantan	 Affected by sulfur, reducing or sulfurous gas, 50c, and Ris 1. Oxiditions and reducing authorshores have little effect on accuracy. Best used in deplacement of surface, good up to Reimanner to oxidation: good up to
Copper vs. Constantag	400°C, but peor above 700°C. 3. Resistance to reducing atmosphere: mod (up to 400°C.) 4. Protect from ovvgen, moisture, sulfur 1. Subject to oxidation and alternation above 400°C, due to copper, above 600°C, due to Constantian wire. Contamination of copper affects calibration areastly.
Chromel-P vs. Constantan	2. Resistance to oxidizing atmosphere: cood 3. Resistance to reducing atmosphere: acod 4. Requires protection from acid fumes 6. Chromel attacked by sulfurous atmosphere 7. Resistance to oxidation: good 8. Resistance to reducing atmosphere: good 9. Resistance to reducing atmosphere: good

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

Table 3: Methods of Joining Thermocouple Wires

Type of thermocounse	Mernoa or pating	z.ux
Placedia vs. ; lacenim-recétura.	Onj gas hamir wei i	Noce
	Elertino-arc weld	None
Caromel-P vs. Alumei	. Oxyucety lene or vity gas flame.	
	weld.	500000
	Liectric-are well	None
	piiver solder	Borax
)	Fleetric-resistance wend	Yor.
lrog vs. Constantan	Oxygretylene or oxygas fiame	
	- चर्चार्य	i Buorite
	Electric-arc weilf	None
	Silver solder	Bores
	i Solt solder	Post n
41	Lieutric-resistance weld	Some
Copper vs. Constantan .	Fleetme-are a mid	Non-
	Silver solder	Boeat
•	e of a solute:	Louis
Guilland I va. Constantan	I Ovvacus, no ef grades audie	Barat
	wel!	. Buorier
	Electric-ace weld	`rone
_	lighter solder	Doras

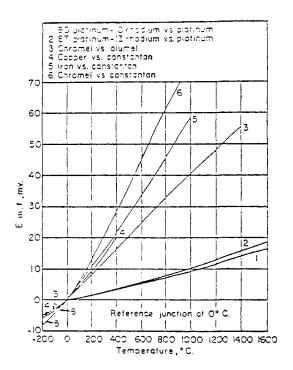
(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

Table 4: Recommended Maximum Operating Temperature of Thermocouple Protecting Tubes

Type of tube	. Recommence, max. tem:			
	•C.	*F.		
Meta, Tu:	ිස			
High silicon tron	425	800		
Desiral est steel	550	1000		
Carbon steel	550	1000		
Cast Iron	700	1300		
Wrought iron	700	1300		
18 Cr-8 Ne stainless steel.	950	1800		
28 Ur iron	1100	2000		
Unrothel T.	1000	2000		
Nichtome. i	1100	2000		
-21 Cr.51	1100			
40 CI-34 MI-40 Le (Incolos)	1100	2000		
Inconel	1260	2000		
		2300		
Ceramic Tu				
Fused silica.	1050	1900		
Fire clay	1550	2300		
illimanite	1550	Z200		
Mullite	1550	2800		
ilica	1600	2900		
ilicon curbide	1650	3000		

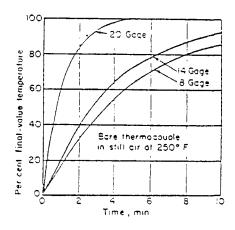
(Perry's Chemical Engineers' Handbook, 4th Edition, p.22-7)

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:

DWELL _ Volume of combustion chamber
TIME Volumetric flow rate of gas thru chamber
where,

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 $100~{\rm FT}^3$ and an after burn chamber of $2000~{\rm FT}^3$, fuel rate = $10,000\#/{\rm hour}$, air rate = $90,000\#/{\rm hour}$, primary chamber temperature - $3000^{\rm OF}$, afterburner temperature = $2500^{\rm OF}$, chamber pressure = $5~{\rm psig}$ = $20~{\rm psia}$

Vol Furnace = $100 \text{ FT}^3 + 2000 \text{ FT}^3 = 2_{100} \text{ FT}^3 \text{ at } T = 2500^{\circ}\text{F}$

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

then,

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

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

Density = Ambient Temperature (${}^{C}K$)

13.1 X Combustion Temperature (${}^{C}K$)

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

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:

$$\frac{\text{Cco}_2}{\text{Cco} + \text{Cco}_2}$$
 x 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 \pm 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 \pm 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) <u>Waste burn.</u> 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, CO₂ and O₂ 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 $_{\rm X}$, total chlorinated organic content (RCL) and PCB chemical substances, should be conducted as specified below.

5.2.1 CO, CO_2 , O_2

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 HCl

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 Methods of Air Sampling and Analysis, 2nd Edition, and in Standard Methods for the Examination of Water and Wastewater. Both are publications of the American Public Health Association.

5.2.3 RCL and PCBs

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.

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.

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Attachment A

Tentative Method of Testing for Polychlorinated Biphenyls in Spilled Material

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

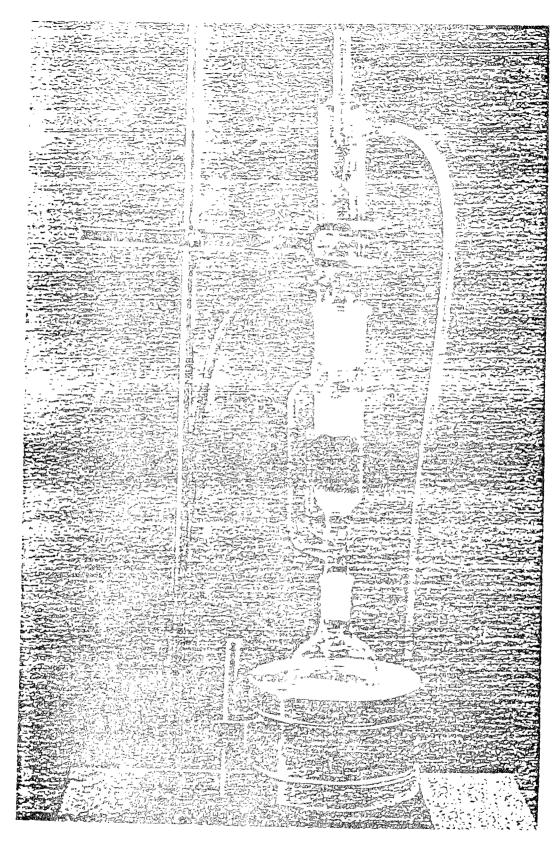
Any excess liquid is decanted and the sample is spread in a pyrex dish (8" wide x 12" long x 2" deep). The sample is air dried at room temperature for about 4 to 5 days in a contaminate free area. The dried sample is then ground with a procelain mortar and pestle to a uniform particle size.

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.)



Soxhler 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/1. Trace quantities of PCB's are often masked by background which usually occur in the samples.
- 9.5 If condition \underline{a} exists, quantitatively determine the organochlorine pesticides according to (1).
- 9.6 If condition <u>b</u> exists, PC3's only are present, no further separation or cleanup is necessary. Quantitatively determine the PC3's according to 11. below.
- 9.7 If condition <u>c</u> 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 \underline{d} exists separate the sulfur from the sample using the method outlined in (10.5) 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. Cleanum and Separation Procedures

- 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 funne.

 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

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

15% 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 \pm 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% etherbenzene mixture, assemble reservoir (using spring clamps) and fill with approximately 15 ml of the 0.50% etherbenzene 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 amoul. As the last of the n-hexane reaches the surface of the sodium sulfate, release the air pressure and change the collection amoul.

- 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.
- 10.4.5.2 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 PC3'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 analyting them by gas chromatography to determine the following:
 - The fraction with the first eluting PCB's (those present in 1260),
 - 2) The fraction with the last eluting PC3'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:
 - 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).
 - 5) 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 un
known. Measure and sum the areas of the unknown and the

reference Aroclor and calculate the result as follows:

$$\label{eq:microgram/liter} \begin{aligned} &\text{Microgram/liter} = \frac{\text{[A] [B] [V_t]}}{\text{[(V_i) (V_s)]}} \times \text{[N]} \end{aligned}$$

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

B = Σ of Sample Peak Areas = (mm^2)

 $V_i = Volume of sample injected (µ1)$

V = Volume of Extract (ul) from which sample
 is injected into gas chromatograph

V = Volume of water sample extracted (ml)

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

- 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

 O.1 ng/ul for the Aroclors and O.02 ng/ul 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

RTDDE = 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 .

$$ng/mn^2 = \frac{(ng_i) (\underline{mean weight percent})}{100}$$

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/mm² x Area

Where Area = Area (mm²) of sample peak

ng/mm² = Response factor for that peak measured.

Then add the nanograms of PCB's present in the injection to get the total number of nanograms

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

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

 $V_{\rm S}$ = volume of water extracted (m1)

 V_t = volume of extract (µ1)

V_i = volume of sample injected (µ1)
Ing = sum of all the PC3'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 analyted, 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 14 16 19 21 28 32 [37 40	31.8 19.3 10.1 2.8 20.8 5.4 1.4	15.8 9.1 9.7 9.7 9.3 13.9 30.1 48.8	1 1 2 2 2 2 3 15% 3 10% 3 90% 3
Total	93.3		

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

bStandard deviation of seventeen results as a percentage of the mean of the results.

CFrom GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 2 Composition of Aroclor 1232 (8)

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

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

**DStandard deviation of four results as a mean of the

CFrom GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 3 Composition of Aroclor 1242(8)

RRTª	Mean Weight Percent	Relative Std. Dev. ^b	Number of Chlorines ^C
11 16 21 28 32 37 40 47 54 58 70 78 84 98 104 125 146	1.1 2.9 11.3 11.0 6.1 11.5 11.1 8.8 6.8 5.6 10.3 3.6 2.7 1.5 2.3 1.6	35.7 4.2 3.0 5.0 4.7 5.7 6.2 4.3 2.9 3.3 2.8 4.2 9.7 9.4 16.4 20.4 19.9	1 2 2 2 3 3 3 3 4 3 4 3 4 3 4 3 4 3 4 4 5 5 5 5
Total	98.5		

aRetention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

**DStandard deviation of six results as a percentage of

the mean of the results.

CFrom GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 4 Composition of Amoclor 1248 (8)

RRTa	Mean Weight Percent	Relative Std. Dev.b	Number of Chlorines ^C
21 28 32 47 40 47 54 58 70 78 84 98 104 112 125	1.2 5.2 3.2 8.3 8.3 15.6 9.7 9.3 19.0 6.6 4.9 3.2 3.3 1.2 2.6	23.9 3.3 3.8 3.6 3.9 1.1 6.0 5.8 1.4 2.7 2.6 3.2 3.6 6.6 5.9	2 3 3 3 3 4 10% 4 3 10% 4 4 90% 4 4 5 5 5 10% 5 90% 4 5 90% 5 90% 5 10% 5 5 10% 5 10
Total	103.1		

aRetention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

Description

**Descript

the mean of the results.

CFrom GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 5 Composition of Aroclor 1254 (6)

RRTª	Mean Weight Percent	Relative Std. Dev.b	Number of Chlorines
47 54 58 70 84 98 104 125 146 160 174 203 232	6.2 2.9 1.4 13.2 17.3 7.5 13.6 15.0 10.4 1.3 8.4 1.8 1.0	3.7 2.6 2.8 2.7 1.9 5.3 3.8 2.4 2.7 8.4 5.5 18.6 26.1	4 4 4 25% 7 7 7 8% 8% 8% 8% 8% 8% 8% 8% 8% 8% 8% 8% 8%
Total	100.0		

aRetention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

bStandard deviation of six results as a percentage of the

mean of the results.

CFrom GC-MS data. Peaks containing mixtures of isomers are bracketed.

Table 6
Composition of Aroclor 1260 (8)

	,		
RRTª	Mean Weight Percent	Relative Std. Dev. ^D	Number of Chlorines ^c
70 84 [98 [104	2.7 4.7 3.8	6.3 1.6 3.5	5 5 60%
117 125	3.3 12.3	6.7 3.3	5 60% 6 40% 6 15% 6 85%
146 160	14.1	3.6 2.2	6 6 50% 7 50%
174 203	12.4	2.7 4.0	6 6] 10% 7] 90%
[232 244	9 . 8	3.4	e 10% 6 10% 7 90%
280 332 372 448 528	11.0 4.2 4.0 .6 1.5	2.4 5.0 8.6 25.3 10.2	7 7 8 8 8
Total	98.6		

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

bStandard deviation of six results as a mean of the results.

CFrom GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

dComposition determined at the center of peak 104.

eComposition determined at the center of peak 232.

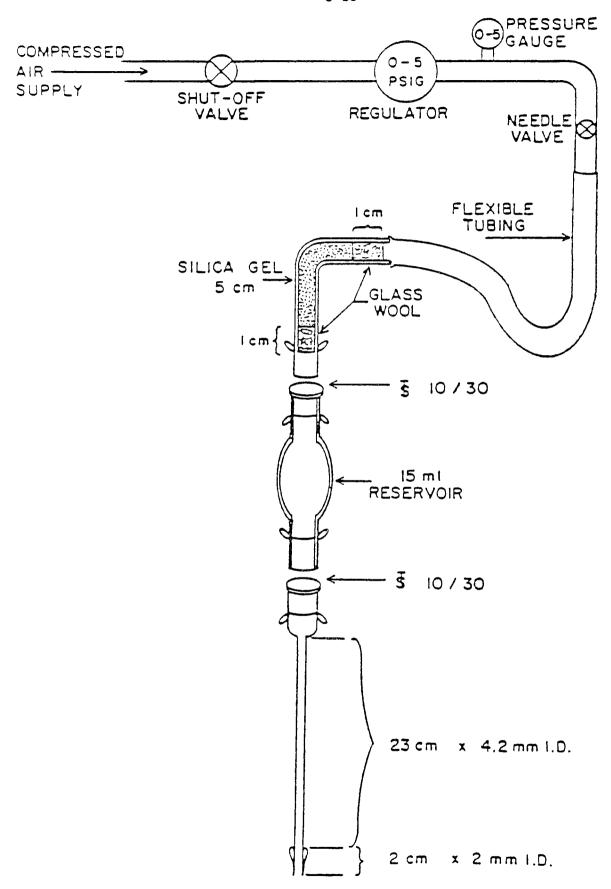
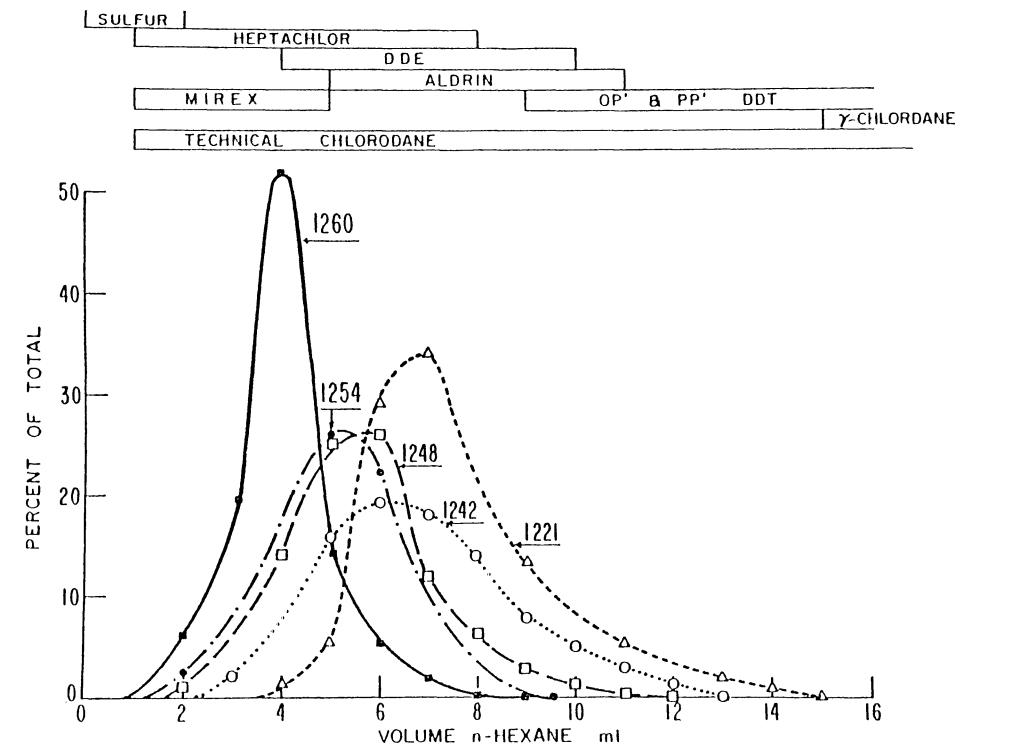


FIGURE 1. MICROCOLUMN SYSTEM



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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) (8).

 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.
 - 15.3.3 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 phenol-phthalein 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 Florisi1 = 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.

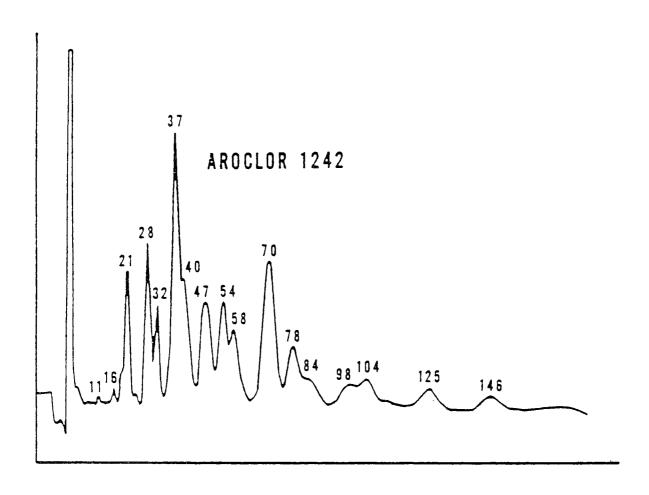


Figure 3. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture

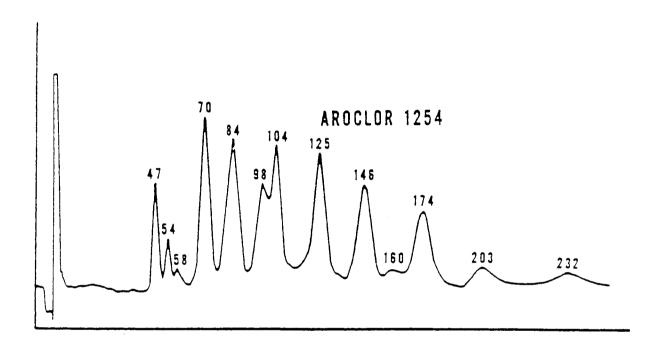


Figure 4. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

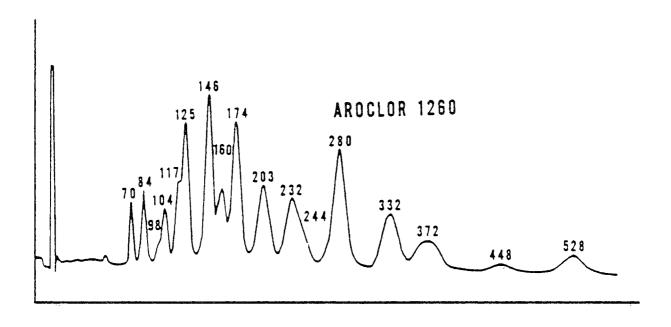


Figure 5. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

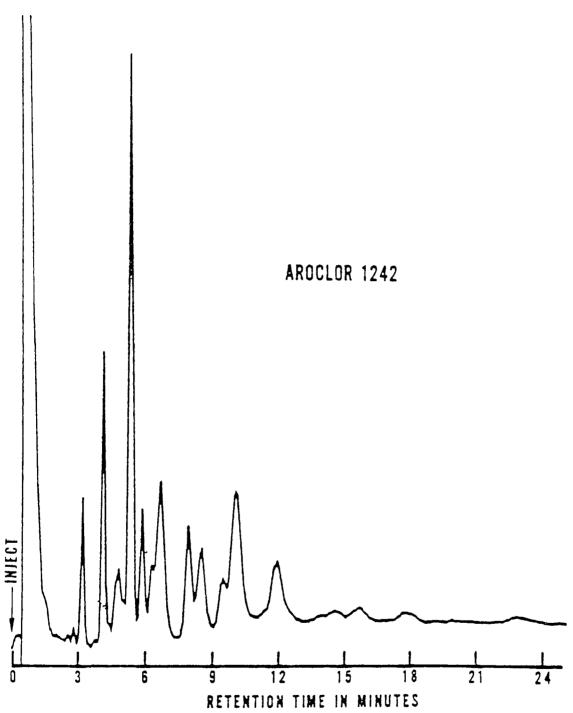


Figure 6. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture

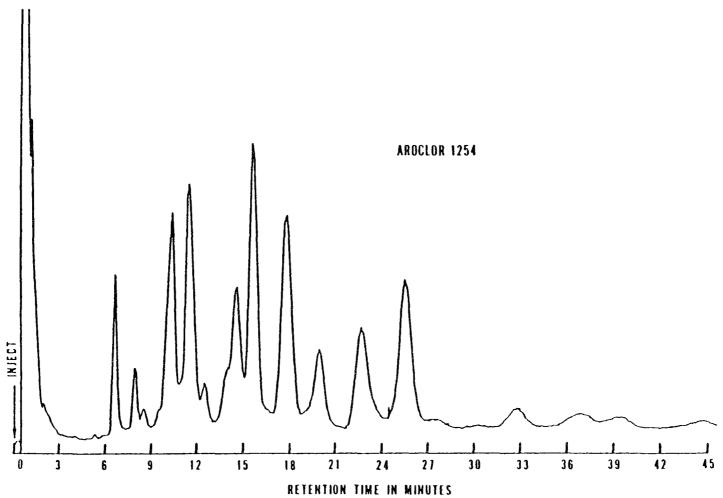


Figure 7. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

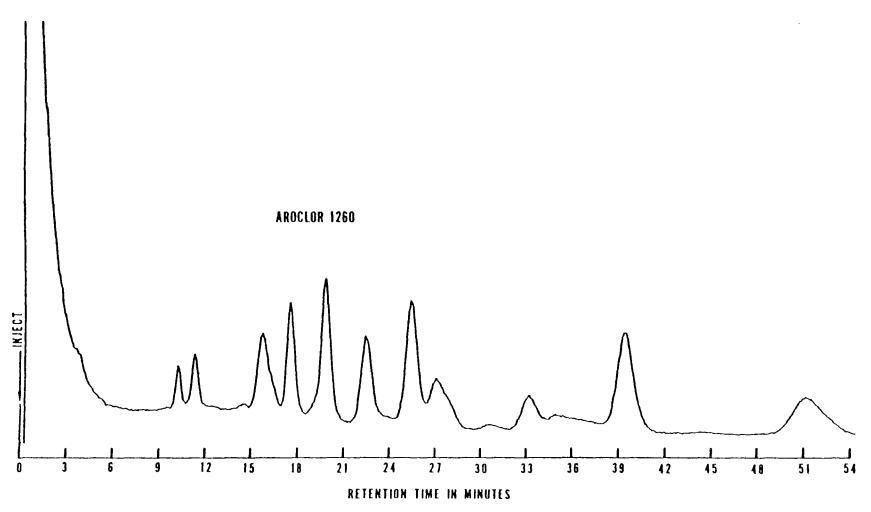


Figure 8. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Mitrogen at 60 ml/min, Column Temperature: 200C, Detector: Electron Capture.

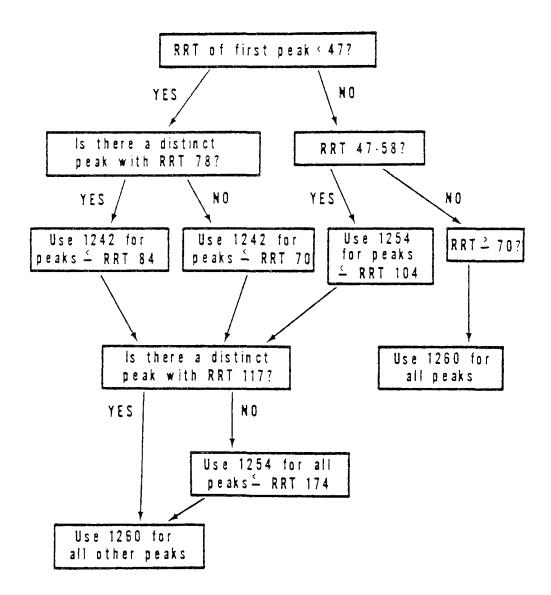


Figure 9. Chromatogram Division Flowchart (8).

Attachment B

Tentative Method of Testing for Polychlorinated Biphenyls in Water

ENVIRONMENTAL PROTECTION AGENCY REGION II EDISON, NEW JERSEY 08817

-- or 2-SA-TS

DAIL January 22, 1976

Polychlerinated Biphenyls in Water.

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, <u>Dynamic Mass Spectrometry</u> Vol. 2, 177-202, Heyden & Son Ltd., 1971, U.K.
- 2.6 E. J. Bonolli, Anal. Chem., 44, 003-000 (1972).
- 2.7 T A. Bellar & J. J. Lichtenberg, ASTM, STP 573, "06-219 (1979).
- 2.8 J. W. Eichelberger, L. H. Harris and W. L. Budde, Anal. Chem. Go., 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 chromatograph mass spectrometry. Either electron impact (70 eV) or chemical ionization (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 FCB'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 0 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 a start collecting data. Methane $(750~\mathrm{u})$ 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} Λ/V sensitivity (10^{-8} Λ/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

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 isotopy 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 λ -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 λ roclor 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 Cl₃ 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 Cl₃ 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 \pm 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-101 Added	.6, ug/l Found	Recovery Per Cent of Added Amount
В	8/21	0	<1	-
L	8/21	5.4	6.4	119
I	8/21	51.4	53	103
Н	8/21	446	447	100
H-2	8/26	5.9	6.6	112
I-2	8/26	91.2	8 ੪.5	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 $\rm Na_2SO_4$ is dried for a minimum of 24 hours at $105^{\rm O}\rm C$. 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 $105^{\circ}C$.

B. F. Dudenbostel
Chemist

Attachment C

Determination of CO Emissions from Stationary Sources

METHOD 10—DETERMINATION OF CARBON MON-OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability.

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

1.2 Applicability. This method is appli-

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 1,060 ppm.

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

3. Inter/erences. Any substance having a strong absorption of infrared energy will haterfere to some extent. For example, distimination ratios for water (H_O) and carbon dioxide (CO₂) are 3.5 percent H₂O per 7 pm CO and 10 percent CO₂ per 10 ppm CO, respectively, for devices measuring in the 1500 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 H₂O per 25 ppm CO and 10 percent CO₂ 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 ±6 percent of span after calibration.

5. Apparatus.

5.1 Continuous sample (Figure 10-1).

5.1.1 Probe. Stainless steel or sheathed Pyrex's 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 ft).

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

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.

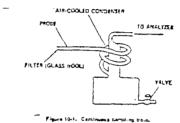
5.3 Analysis (Figure 10-3).

5.3.1 Carbon monoride 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.

53.4 Filter. As recommended by NDIR manufacturer.



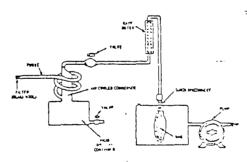


Figure 10-3, Integrated pro-Campling Visits,

5.3.5 CO, removal tube. To contain approximately 500 g of ascarite.

6.3.6 Ice water bath. For ascarite and silica gel tubes.

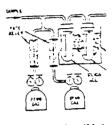
5.3.7 Value. Needle valve, or equivalent, to adjust flow rate

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

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

6. Reagents.

of Colibration gase of CO in nitrogen (N prepurified grade of N tional concentrations mately to 60 percent a span concentration so the applicable source The calibration gase the manufacturer to of the specified concer



8.2 Silica gel. Indica dried at 175 °C (347 °C) 6.3 Ascante. Comme 7. Procedure. ——

7.1 Sampling.
7.1.1 Continuous equipment as shown sure all connections probe in the stack a purge the sampling lyzer and begin dra analyzer. Allow 5 m to stabilize, then recing as required by 117.2 and 8). CO₂ condetermined by using grated sample proces

Test	
	Cloc

9. Calculation—Commonoxide in the stack

where:

 $C_{\text{CO}_{\text{NDIR}}} = \text{conce}$: $C_{\text{CO}_{\text{NDIR}}} = \text{conce}$: $E_{\text{CO}_{\text{NDIR}}} = \text{conce}$: $E_{\text{CO}_{\text{NDIR}}} = \text{conce}$:

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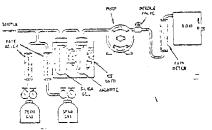
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NDIR

6.1 Calibration gases. Enown concentration of CO in nitrogen (N₂) for instrument span, prepurified grade of N₁ 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.



Puparo 10-1. Analytical employers.

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, content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or

by weighing the ascarite CO, removal tube and computing CO, concentration from the gas volume sampled and the weight gain of the tube.

7.12 Integrated sampling. Evacuats 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, content of the gas may be determined by using the Method 3 integrated sample procedures (38 FR 24886), or by weighing the ascarite CO, removal tube and computing CO, 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 N₂ 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 CO₃ removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the macufacturer's procedures using, respectively, nitrogen and the calibration gases.

Train 10-1.—Field data

Comments:									
Operator meaning									
Clock time	Rotameter setting, liters per minute (cubic feet per minute)								
enterprise (S. 1927). And the contrast of the									

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

 $C_{\text{CO}_{\text{otab}}} = C_{\text{CO}_{\text{NDIR}}} (1 - F_{\text{CO}_2})$ equation 10-1

where:

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

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

F_{CO₂} = volume fraction of CO₂ in sample, i.e., percent CO₂ from Orsat analysis divided by 100.

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- 10. Bibliography.
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- 30.2 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.
- Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton,
- 10.6 UNOR Infrared Gas Analyzers, Bendir Corp., Ronceverte, West Virginia.

A. Performance Specifications for NDIR Carbon Monoride Analyzers.

Range (minimum)	0-1000ppm.
Output (minimum)	0-10mV.
Minimum detectable sensitivity	20 ppm,
Pise time, 90 percent (maximum)	30 seconds.
Foll time, 90 percent (maximum)	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	
Precision (minimum)	± 2% of full scale.
Not e (maximum)	± 1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO,-1000 to 1, H2O-500 to

B. Definitions of Performance Specifica-

-The minimum and maximum 1.73.174 agarement limits.

Output-Electrical signal which is proportonal 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

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 SUL-FIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and applicability.

1.1 Principle. Hydrogen sulfide (H.S) is collected from the source in a series of midget impingers and reacted with alkaline cadmium hydroxide [Cd(OH),] to form cadmium sulfide (CdS). The precipitated CdS is then dissolved in hydrochloric acid and absorbed in a known volume of lodine solution. The iodine consumed is a measure of the H,S content of the gas. An impinger containing hydrogen peroxide is included to remove SO, 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 the performance standards. 2. Apparatus. 2.1 Sampling train.

2.1.1 Sampling line-

-6- to 7-E Teflon ! tubing to connect sam; sampling valve, with provision to prevent condensation; A pri ing valve prior to the Teffon : 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 to 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 ft'/min).

2.19 Graduated cylinder-25 2.1.10 Resembles—To measure pressure within #2.5 mm (0.1

2.2 Sample Recovery. 22.1 Sample container-500-2

pered lodine flask. 222 Piperte-50-mi volumet:

2.23 Beakers-250 ml 2.2.4 Wash bottle-Glass.

23 Analysis. 2.3.1 Flask-500-ml glass-sto;

flask. 2.2.2 Burette-One 50 ml 2.3.2 Flask-125-mi contral.

3. Reagents. 3.1 Sampling.

3.1.1 Absorbing solution-Ca droxide (Cd(OH),)—Mix 4.3 g c fate hydrate (3 CdSO,8H,O) sodium hydroxide (NaOE) tilled water (H_O). Mix well.

Note: The codmium hydroxic this mixture will precipitate as pension. Therefore, this solut! 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 coid soluti percent by weight-mix 230 m

¹ Mention of trade names or s ucts does not constitute endors-Environmental Protection Agenc

Attachment D

Gas Analysis for ${\rm CO_2}$, ${\rm O_2}$, Excess Air, and Dry Molecular Weight

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June 14-19, 1970.)

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Probes. Prepared by the University of Windsor for the Ministry of the Environment, Toronto, Canada. February 1974.

LTBOD 3—GLA ANALTHIS FOR CARRON DIOXDE, VITORN, EITHMARR, AND DRIMOLECULAR WEIGHT

1. Principle and Applicability

1.1 Principle. A gas sample is attracted from a stack, by one of the following methods: (1) interleonate, property of the property of the sampling; (2) single-point, interested sampling; or (3) midd-point, interested sampling. The gas sample is analysed for person carbon distrile (CO), purnant expect (CO), it a dry molecular weight determination is to be made, either an Ornation a Fittle I analyster may be used for the analysis: for atress air or emission rate correction factor determination, an Ornat analyser must be used.

1.2 Applicability. This method is applicable for de-remining CO; and O; concentrations, stress air, and dry molecular weight of a sample from a gas stream of a fossilined combustion process. The method may such be applicable to other processes where it has been determined that compounds other than CO; O; CO; and introgram 1.1 Principle. A gas sample is extracted from a stack.

that compounds other than CO₂, O₃, CO₃ and a thegra (N₁) are not present in concentrations sufficient to results.

Other methods, as well as modifications to the procedure described berein, are also applicable for former and of the spove determinations. Examples of specific mathematical and modifications include. (I) a multi-point temporal gradient of any point temporal and brain and present analyses to analyze individual stab samples octained at each point (1) a method using CO₂ or O₂ and sportionmetric calculations to determine dry molecular weight and excess aim (3) assigning a value of 30.0 for dry molecular weight, to be und actual measurements, for processes burning alternative social, or oil. These methods and modifications may be used, but are subject to the approval of the Administration.

As an alternative to the sampling apparatus and systems described berein, other sampling systems (e.g. liquid dispincement) may be used provided such systems are capable of obtaining a representative sample and animalining 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 (Figurs 3-1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicials glass (bound a should be equipped with an in-stack or out-stack litter to remove particulate matter (a plus of glass wool is satisfactory for this ourpose). Any other material inert in Ot, COt, CO, and Ni and resistant to temperature at sampling conditions may be used for the probe; samples of such material are As an alternative to the sampling apparatus and sys-

be used for the probe; stamples of such material are aluminum, copper, quartz glass and Tellon.

1.1. Pump. A one-way squeets only, or equivalent, is used to transport the gus sample to the analyzer.

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Proba A probe such as that described in Section 11.1.5 and 11.

I liention of trade names or specific products does not constitute endorsement by the Environmental Protection non Asency.

RULES AND REGULATIONS

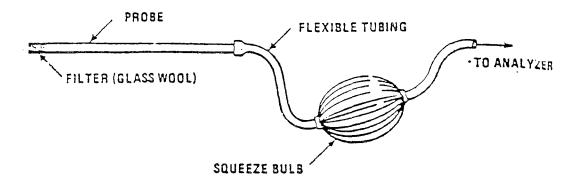


Figure 3-1. Grab-sampling train.

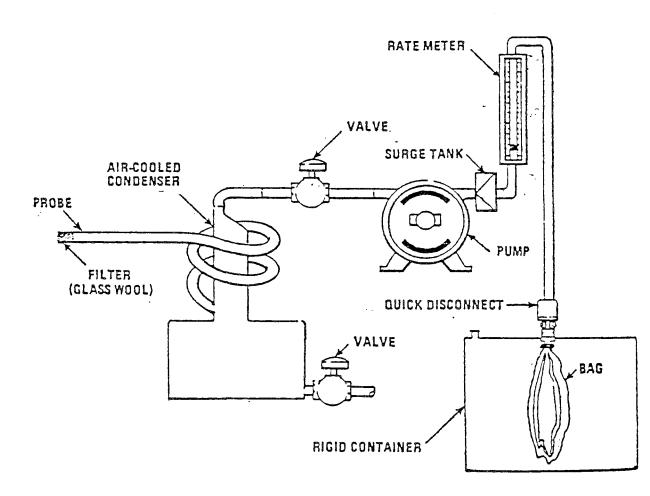


Figure 3-2. Integrated gas-sampling train.

RULES AND REGULATIONS

2.2.2 Condenser. An air-cooled or water-pooled condenser, or other condenser that will not remove O_k CO_3 , CO_3 and N_3 may be used to remove atom moisture which would interfere with the operation of the pump and flow meter.

2.2.3 Vaive. A needle vaive is med to adjust sample

2.2.3 Vaive. A needle valve is timel to acquire mapor gas flow rote.

2.2.4 Primp. A leak-free, disphraems-type primp, of equivalent, is used to transport sample cas to the ficable but, install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the discount of the estimates.

big. Install a small surge tank between the pump and rate meter to eliminate the pulsation affect of the displant mump on the rotameter.

11.3 Rate hieter. 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 cm²/min is surgested.

12.16 Flexible Bag. Any leak-free pissite e.g., Tediar, Mylar, Tedon) or plastic-coated attimizing e.g., aluminized Mylar) bag, or equivalent, having a capacity of the test run, may be used. A capacity in the range of 50 to 90 tiers is suggrested.

To leak-check the use, connect it to a water manometer and pressuring the bag to 3 to 10 cm. Hr.O. 2 to 4 in. Hr.O. Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressuring the bag to 3 to 10 cm. Hr.O. 10 to 4 in. Hr.O. and allow to stand overnight. A defauled bag indicates a leak. An alternative leak-check method is to pressuring the bag to 3 to 10 cm. Hr.O. 12 to 4 in. Hr.O. and allow to stand overnight. A defauled bag indicates a leak.

2.2.7 Presoure Cauge. A water-filled U-table manometer, or equivalent, of a basic check.

2.2.3 Vacuum Gauge. A manury manometer, or equivalent, of at basis the min. Fig. 10 in. Eg. 1s used for the sampling train leak-check.

squimient, of at tests for min the sampling train leak-check.

2.3 hnalysis. For Oracle and Fyrite ar liyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise

specified regard.

2.3.1 Dry Molecular Weight: Determination. An Orsal analyzer of Fyrite type combustors gas analyzer may be

used.

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

3. Dry Moleco for Weight Determination

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

Single-Point, Grab Sampling and Analytical

2.1.1 The sampling point in the duct shall either be 3.1.1 The sampling point in the duct shall either be at the control 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 sheed of the analyzer are tight and leat-tree. If an Ornat analyzer is used, it is recummended that the analyzer be leaked-checked by following the procedure in Section 3; however, the leak-check is opnomial.

check is opnoral.

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 as sample into the analyzer and immediately analyze it for percent Co and percent O. Detatmine the percentage of the gas that is Ns and Co by subtracting the sum of the percent Co and percent Os from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.14 Researt the sampling analysis and calculation.

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 dider from their mean by no more than 0.3 gg-mois (0.3 lis/lb-mois). Average these three molecular weights, and report the results to the nearest 0.1 gg-mois (lis/lb-mois).

3.2 Single-Point, Integrated Sampling and Analytical Proceedings.

3.2 Single-Point, Integrated Sampling and Analytical Procedure.

2.2.1 The sampling point in the duct shall be located asspecified in Section 3.1.1.

3.2.2 Leak-check (optional) the flexible beg as in Section 2.2.5. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by piacing a vacuum gauce at the condensar inlet, pulling a vacuum of at least 250 mm Hz (10 in. Hz), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.2 infinite. Evacuain the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling prior, purper 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. Colicition of at least 30 liters (1.00 (14) of sample gas is recommended: however, smaller volumes may be ableded if desired.

tion. Collection of at least 30 liters (1.09 ft) of sample case 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 3 hours after the sample is taken, analyze it for percent (10) and percent O₂ using eitner an Orsat analyzer of a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leakmosk described in Section 5 be perferned before this determination; however, the che k is optional. Determine the percentage of the gas that is Nagari CO by subtracting the sum of the percent CO and percent O₃

from 100 percent. Calculate the dry molecular weight as indicated in Section 6 3.

3.2.5 Repeat the analysis and calculation procedures mult the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 mult the individual dry molecular weights for any three snalyses duller from their mean by no more than 0.3 gg-mois (0.3 lb/b-mois). Average them three molecular weights, and report the results to the nearest 0.1 gg-mois (0.1 lb/lb-mois).

3.3 Multi-Point, Integrated Sampling and Applicated Procedure.

Procedure.

3.11 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less then 0.51 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 used for all other cases. The traverse points shall be used for all other cases. The traverse points shall be used for all other cases. The traverse points shall be used for all other cases.

3.3.2 Follow the procedures outlined in Sections 3.3.2 through 3.2.5, except for the following: traverse all mmpling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-2.

4. Emission Rate Correction Factor or Excess Air Deter-

Note.—A Fyrite-type combustion gas analyzer is not acceptable for agoest air or emission rate correction factor determination, unless approved by the Administrator. If both percent CO₂ and percent O₃ are measured, the analytical results of any of the three procedures given below may saw be used for casculating the dry molecular

Each of the three procedures below shall be used only that not the time procedures below that be used only per specified in an applicable subpart of the standards, he use of these procedures for other purposes must have ecute prior approval of the Administrator, L. Single-Point, Grab Sampling and Analytical

4.1.1 Single-round, the first sampling point in the duct shall either be at the centroid of the cross-section or at a point po closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the stimulum raine.

to the walls that 1.00 m (all it), unuse other wise specime by the Administrator.

4.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections should of the analyter are tight and leak-free. Leak-check the Ormat analyter ac-cording to the procedure described in Section 3. This leak-check is mandatory.

TIME _	TRAVERSE PT.	Q 1pm	% DEV.ª		
,	·				
			·		
a % DEV = (AVERAGE O - O avg 100 (MUST BE ≤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; purys the sampling inc. Draw a sample into the analyser. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO; or percent O. If excess the is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 4.1.4 and 4.1.5, for percent CO; O;, and CO; (2) determine the percentage of the gas that is N; by subtracting the sum of the percent CO; percent O; 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; O; If appliable, CO; O, make repeated peases 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; 4.1.3 Place the probe in the stack, with the tip of the

obtained after three consecutive readings, replace the absorbing solution.)

4.1.5 After the snalysis 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 snalyzer must pass this leak test before and after the analysis. Nove.—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 to ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO₂ or O₂ is required, it is recommended that both CO₂ and O₃ be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.2 Single-Foint, Integrated Sampling and Analytical

Single-Point, Integrated Sampling and Analytical 4.2.1 The sampling point in the duct shall be located as specified in Section 4.1.1.

as specified in Section 4.1.1.
4.2.2 Leak-check (mandatory) the flavible bag as in Section 2.2.6. Set up the equipment as shown at Figure 3.2. Just prior to sampling, leak-check (mandatory) the train by placing a vacuum of at least 12.0 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. Evaceate the florible bast. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purve the sampling line. Next, connect the bag and make sire that all connections are tight and leak free.

4.2.1 Eample 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 politicant emission rate determination. Collect at least 20 liver (1.00 (t) 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 pollutar emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO or opercent O₁ (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-checked (see Section 3) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO₂. O₃, and CO₁ (2) determine the percentage of the gas that is N₁ by subtracting the sum of the percent CO₂ and CO₃; (2) determine the percent CO₄ contait applicable, CO₃, make repeated pusses through each size of the percent goliution until two consecutive readings are the same, Several passes (three or four) should be made between readings, (II constant readings, replace the absorbing solution until two consecutive readings cannot be obtained after three consecutive readings, replace the absorbing solution.

on.)

8 Repeat the analysis until the following criteria

4.2.6 Repeat the analysis until the following critoria are met;
4.2.5.1 For percent CO₂, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO₂ is greater than 4.0 percent or (b) 0.2 percent by volume when CO₃ is less than or equal to 4.0 percent. Average the three acceptable values of percent CO₃ and report the results to the reasest 0.1 percent.
4.2.4.2 For percent O₃, repeat the analytical procedure much the results of any three analytical procedure.

than and Thereent by volume when Ce is less than 15.0 percent O: and report the results to the memory of

percent.
4.2.d.3 For parcent CO, repeat the analytical process dure until the results of any three analyses duffer 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.
4.17 After the analysis is completed, 'mak-check (mandatory) the Orsat analyter once around as described in section 5. For the results of the qualysis to be valid, the Oraci analyte must near this leak test before and after the analysis. Note Although in most instances only CO₂ or O₂ is required, it is recommended that both CO₂ and O₂ be treatured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4 3 Moit.-Point, Integrated Sampling and Analytical

4.3 Moit. 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 lewer points than specified a subject to the approval of the Administrator.
4.3.2 Follow the procedures outlined in Sections 4.2.3 through 4.2.7 except for the following. Traverse all sampling points and sample at each point for an equal length of these Regard sampling data at shown in Fourier

length of time. Becord sampling data as shown in Figure

5. Leas-Check Procedure for Orsas Analyzers

Moving an Orsat analyzer frequently couses it to look, Therefore, an Orsat analyzer should be thoroughly leak-checked on site before the due gas sample is introduced into it. The procedure for leak-checking in Orsat analyzer

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

stopcock.
Raise the leveling bulb sufficiently to bring the substituted portion of pipette stopcock.

3.1.2 Raise the leveling bulb sufficiently to bring the confining liquid measons onto the studieted portion of the burstle and then close the manifold stopcock.
3.1.3 Record the mealisms position.
3.1.4 Diserve the incursion in the burstle and the liquid level in the pipette for movement over the next 4

midutes.
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 capitlary inding during this

below the bottom of the capitlary inding during this 4-minutelinterval.

5.1.5.2 The medicus in the burette must not change by more than 0.2 mi during this 4-minutelinterval.

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

6. Calculations

Nomenclature.

6.1 Nomenclature.

Maw Dry molecular weight, g/g-mole (ib-ib-mole).

7.EA = Percent excess air.

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

7.CO = Molecular weight of No for (divided by 100.).

7.CO = Molecular weight of CO; divided by 100.

7.CO = Molecular weight of CO; divided by 100.

7.CO = Molecular weight of CO; divided by 100.

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

$$\% EA = \left[\frac{\% O_2 - 0.5\% CO}{0.204 \% N_1 (\% O_2 - 0.5\% CO)} \right] 100$$

Note.—The equation above assumes that ambient air is used as the source of O₁ and that the fiel does not contain appreciable amounts of N₁ as do coke own in blast furnace gases). For those cases when appreciable amounts of N₁ are present (coal, oil, and natural gas ado not contain appreciable amounts of N₁ or when oxygen enrichments is used, alternate methods, moject to approval of the Administrator, are required.

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

Equation 3-2

Note.—The above equation does not consider aron 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. Bulliography

7. Bioliography
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METEOD 4—DETERMINATION OF MOSSICILE CONTINUE CONTINUES C

1. Principle and Applicability

1.1 Principle A gas sample is extracted at a costan rate from the source: mosture is removed from the so-ple stream and determined either volumetricity gravimeuncaily.

gravimetrically.

1.2 Applicability. This method is applicable in determining the mustifure content of stack got.

Two procedures are given. The dist is a related method, for accurate determinations of mosture colon. method, for accurate determination or moralized only age accord is an approximation method, which provide securates of percent moralizes to administrate tooley. estimates of percent monsture to such setting tooleight sampling rates prior to a politicant emission means that described being mention. The approximation method described being is only a suggested approach; ulternative mean is approximations the monsture content, e.g., drying the west bulb—try bulb techniques, condensation fedingles. ston hiometric culculations, provious expenence, etc. also acceptable

stockhometric calculations, previous experience, etc.
are also acceptable.

The reference method is often conducted similars musty with a polluthat emission measurement run whe is, calculation of permat testimeter, pollutink emissions, etc., for the run shall be based upon the religion for reference method or its equivalent; these chellians shall not be based upon the results of the approximation method, unless the approximation method, unless the approximation method, unless the approximation method is slower, in the mission of the Administrator, U.S. Environmental Protection Agency, to be crawdle of vielding really within 1 percent II,0 of the reservice method.

Note.—The reference method may yield questionable within a percent II,0 of the reservice method results when accorded to saturated gas streams of account of the mounture content shall be made uniquently with the reference method, a second designation of the mounture content, a second designation of the mounture content. Attach a temperature sensor (capable of measuring to =1° C (F) to the reference method traverse; calculate the stack gas temperature. Next, determine the mounture production at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average tax gas temperature. Next, determine the mounture production of the other than a population production of the chart, or (2) using sample valor from the sacuration vapor pressure tables. In cases where the psychonomy chart or the sacuration of the process, silend methods, subject to the approval of the Adminished. miethods, subject to the approval of the Adminimum, shall be used.

2. Reference Method

The procedure described in Method 5 for determining

noisture content is acceptable as a reference method.

2.1. Apparatus. A schematic of the sampling lunused in this reference method is shown in Figurely All components shall be maintained and calibrate 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 <u>Sampling Train</u>. 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 \leq 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,

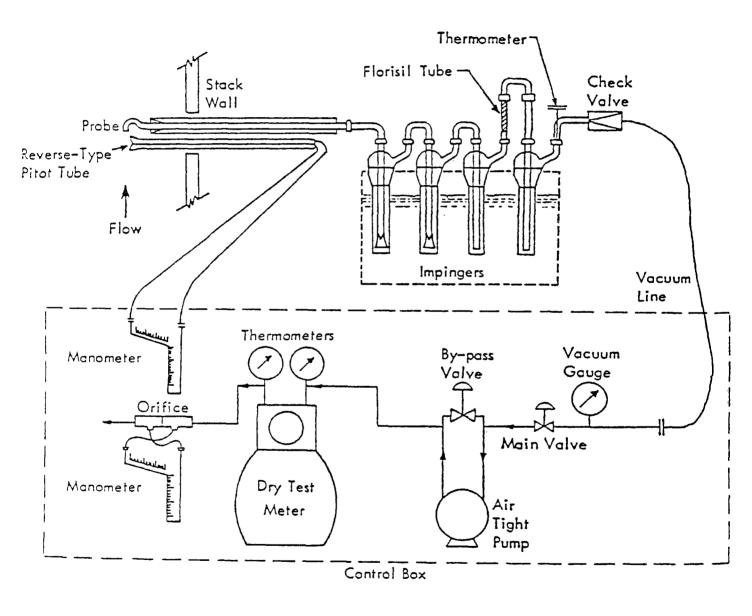


Figure A-1. PCB Sampling Train for Incinerators

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 (\sim 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 $\text{FEP}^{\mathfrak{D}}$ wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.
- 5.2.3 Sample storage containers--Glass bottles, l liter, with $TFE^{\textcircled{3}}$ -lined screw caps.
 - 5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.
 - 5.2.5 Aluminum foil--Heavy duty.

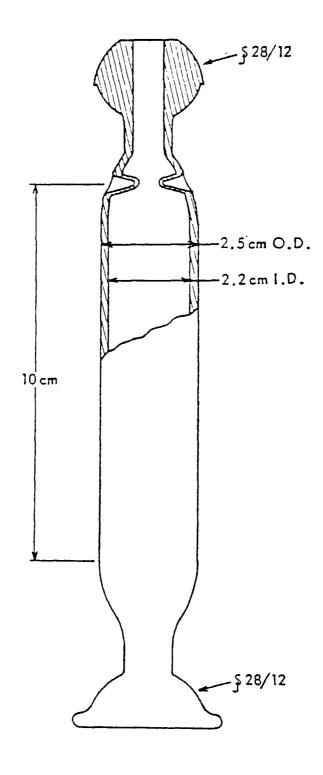


Figure A-2. Florisil Adsorbent Tube

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 $\frac{1}{3}$ condenser, 24/40 $\frac{1}{3}$ 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 $^{\textcircled{@}}$ -glass syringe--1 ml, Hamilton 1001 TLL or equivalent with Teflon $^{\textcircled{@}}$ 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 $^{\otimes}$).
 - 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 $650\,^{\circ}\text{C}_{\cdot}$

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 hexanerinsed glass containers with $TFE^{\mathfrak{D}}$ -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 hexanerinsed glass containers with TFE@-lined screw caps.

- 6.3.4 Sodium sulfate (Na₂SO₄)--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 (HC1) 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 <u>Sampling</u>. 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 $\rm m^3/min$ (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 \pm 0.02 coefficients ($C_{\rm p}$), and when sampling in air or a stack gas with equivalent density (molecular weight, $\rm M_d$, equal to 29 \pm 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 $\rm C_{\rm p}$ and $\rm M_{\rm d}$ 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.

PLANT
DATE
SAMPLING LOCATION
SAMPLE TYPE
RUN NUMBER
DPERATOR
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 AH
C FACTOR
PROBE HEATER SETTING
HEATER BOX SETTING
REFERENCE Ap

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY_____ MINUTES

TRAVERSE POINT NUMBER	CLOCK TIME (24 h) TIME, min	GAS METER READING (V _m), II ³	VELOCITY HEAD (Δp _s), in, H ₂ 0	ORIFICE PRESSURE DIFFERENTIAL (AH), in, H ₂ O)		TEMPERATURE	DRY GAS METER TEMPERATURE		PUMP VACUUM, In. Hg	SAMPLE BOX TEMPERATURE.	IMPINGER TEMPERATUR::
				DESIRED		(T _s)."F	INLET (Tm in).°F	OUTLET (T _{m out}).°F	ш. н	°F	'
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COMMENTS

Figure A-3. Field Data Sheet

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 <u>Sample recovery</u>. 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 $TFE^{\textcircled{3}}$ -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 $0.0057~\text{m}^3/\text{min}$ (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), pg.
- G_s = Total weight of PCBs (as DCB) in sample, μg .
- C_s = Concentration of PCBs in stack gas, $\mu g/m^3$, 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 (ft²).
- $B_{\rm ws}$ = 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 $Hg-m^3/^{\circ}K-g-mole$ (21.83 in. $Hg-ft^3/^{\circ}R-lb-mole$).
 - 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).
- $V_{m(std)} = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).$
- $V_{w(std)} = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).$
 - $V_{+} = Total volume of sample, ml.$
 - 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

$$V_{w(std)} = V_{lc} \frac{\rho_{w}}{M_{w}} \frac{RT_{std}}{P_{std}} = K V_{lc}$$
 Equation A-2

where $K = 0.00134 \text{ m}^3/\text{ml}$ for metric units = $0.0472 \text{ ft}^3/\text{ml}$ for English units

9.5 Moisture content

$$\frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$
 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.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3}$$

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.

$$C_s = K \frac{G_s}{V_{m(std)}}$$

Equation A-5

where
$$K = 35.31 \text{ ft}^3/\text{m}^3$$

9.7 Isokinetic variation

9.7.1 Calculations from raw data.

$$I = \frac{100 \text{ T}_{s} \left[\text{K V}_{1c} + (\text{V}_{m}/\text{T}_{m}) (\text{P}_{bar}) + \Delta \text{H}/13.6 \right]}{60 \text{ } \text{V}_{s} \text{ } \text{P}_{s} \text{ } \text{A}_{D}}$$

Equation A-6

 $K = 0.00346 \text{ mm Hg-m}^3/\text{ml-}^{\circ} \text{K for metric units}$ = 0.00267 in. $Hg-ft^3/ml-^{\circ}R$ for English units

9.7.2 Calculations from intermediate values.

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

$$= K \frac{T_s V_m(std)}{P_s V_s A_n \theta (1-B_{ws})}$$
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 <u>PCB verification</u>. 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

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Attachment F

Determination of Nitrogen Oxide Emissions from Stationary Sources

13.5 Sultatic Acid Standard, 0.0100 N. Parthase or indudus to ±0.0002 N arsunst 0.0100 N NaOR which a premounly been standardized against polarinum id pittaists (primary standard grads).

Procedure.

4.1 Samplins.
4.1.1 Preparation of collection train. Measure 15 ml of peront isopropassed into the midget bubbles and 15 lol 3 remain hydrogen peroxide into each of the first midget impungers. Leave the first midget impunger y Assemble the train as shown in Figure 6-1. Adjust the center to a temperature sufficient to prevent water themsion. Place cruined ice and water around the ndenation. Place cruined ice and water around the

Leak-check procedure. A leak check prior to the mpling run is optional; however, a leak check after the mpling run is mandatory. The leak-check procedure is

appuar run is mandatory. The leak-check procedure is richiror:
Who the probe disconnected, place a vacuum gauge at while to the bubbler and puil a vacuum of 250 mm plus.) His plug or plach off the outlet of the flow meter, at then turn of the pump. The vacuum shall remain table for at least 30 seconds. Carefully release the round gauge before releasing the flow meter end to revent back flow of the impurger fluid.

sum game before releasing the flow meter end to result back down of the impurger fluid.

Other lack check provedures may be used, subject to be approved of the Admiration, U.S. Environmental rotetion Agency The procedure used in Method 5 is so unable for dispursors pumps.

413 Sample collection. Becord the initial dry gas per resding and he ometric pressure. To begin sampling, position the it of the probe at the sampling point, onset the probe to the bubbler, and start the pump, ident the sample flow to a constant rate of approximately 10. Use from a "classed by the rotameter. Samain this constant rate (= 10 percent) during the intre sampling run. Take resdings (dry gas meter, imperitures as dry gas inetar and at impirizer outlet and ris mater) at least every 5 minutes. Add more ice during the run is keep the temperature of the gases leaving the last impirizer on 20° C (55° F) or less. At the condition of each run, turn of the pump, remove probe from the stack, and record the first readings. Conduct a leak back as in Section 4.1.2. (This leak check is manched to the sax is found, void the test run. Drain the lee leaft, and purge the remaining part of the train by draw-section and each run below the remaining part of the train by draw-section and content at those of the section of 1.5 minutes.

tory.) Is asked in found, void the test full. Drain the lies had had pured 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 error midget impinger with 15 mi of 3 persons EAS. The tester may opt to simply use ambient air, without purification.

on to simply use ambient air, without purification.

12 Sample Recovery, Disconnect the impingers after puring, Discard the contants of the midget bubbler. Pour the contents of the midget impingers into a leak-dree polyethylene bottle for impressing these with deionized, drilled water, and add the washings to tree same storage container. Mark the finial level, Seal and identify the ample container. mmois container.

sample container.

43 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 nodicesole amount of leakage his occurred, either void the sample of the methods, subject to the approval of the Administrator, to correct the final results.

Transfer the contents of the storage container to a libril volument data and diffus to exactly 100 ml with delonized, distilled water. Pipette a 20-ml aliquot of the contents of the storage container to a second state and diffuse to exactly 100 ml with delonized, distilled water. Pipette a 20-ml aliquot of the contents of

with detonized, distilled water. Pipetice a 20-mi aliquot of this solution into a 250-mi Entempeyer flashs, add 80 mi of 100 percent isopropasol and two to four drops of thorin indicator, and titrate to a pink andpoint using 0.0100 N being perchlorate. Repeat and average the titration volume. Run a blank with each series of samples. Repti-cial titrations must agree within 1 percent or 0.2 mi, whichever is larger.

(Norz.—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 lesk check the metering system (drying tube, beedle valve, pump, rotameter, and dry gas meter) as

follows: place a vacuum gauze at the inlet to the drying mos and pull a vacuum of 250 mm (19 m.) fig: plug or pinch off the outlet or the flow meter, and then turn of the pump. The vacuum shall remain viable 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 wat test mater (e.g., 1 liter per revolution) to the inlet of the drying mbs. Mairs three independent calibration runs, using at least five revolutions of the dry gas meter per run. Caicolate the calibration factor, Y (west test meter calibration volume divided by the dry gas meter per trun. Caicolate the calibration befor, Y (west test meter calibration volume adjusted to the same relevance temperature and pressure), for each the same reference temperature and tressure), for each rin, and average the results. If any Y varue deviates by more than 2 percent from the average, the metaring system is unacceptable for use. Otherwise, the the average

age as the calibration factor for subsequent test runs. 5.1.2 Post-Test Calibration Cheez. After each field test series, conduct a calibration cheez as in Section 5.1.1 above, except for the following variations: (a) the leak cheek is not to be conducted, (b) three, or more revoidance to the dry gas mater 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 inimal calibration factor (determined in Section 5.1.1), then the dry gas metar volumes obtained during the test sense are acceptable. If the calibration factor deviates by more 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
rollime for each test run.
5.2. Thermometers. Calibrate against mercury-inglass 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 barom-

5.5 Berium Perchlorate Solution, Standardize the bandum perchlorate solution against 25 ml of mandard solution acid to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

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

Nomenciature.

Con-Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dxcm (lb/dsd).

(b)dscf).

N=Normality of barium perchlorate titrant, millioquivalents/mi.

Phose Barometric pressure at the exit orthos of the dry gas meter, mm Hg (in. Hg).

Phose Standard absolute pressure, 760 mm Hg (20.92 in. Hg).

To Average dry gas motor absolute temperature,

"K ("R).

Tou-Standard absolute temperature, 223° K

Tout Standard absolute temperature, 223° K. (323° B).

V=Volume of sample aliquot utrained, ml.

V=Dry gas volume as measured by the dry gas meter, dom (dcf).

V=(mi)=Dry gas volume measured by the dry gas meter, corrected to standard conditions, dxm (dxf).

V=(mi)=Total volume of solution in which the suitor dioxide sample is contained, 100 ml.

V=Volume of barium perchlorate thrant med for the sample, ml (average of replicate thrattons).

Via=Volume of barium perchlorate thrant used for the blank, ml.

130 volume of barium perchlorate titrant used for the blank, mi.
1 Y Dry gas meter-calibration factor.
22 CB = Equivalent weight of sultur dioxide.
6.2 Dry sample gas volume, corrected to standard conditions.

 $V_{m \text{ (aid)}} = V_m Y \left(\frac{T_{\text{aid}}}{T_m}\right) \left(\frac{P_{\text{bar}}}{P_{\text{aid}}}\right) = K_i Y \frac{V_m P_{\text{bar}}}{T_m}$

Equation 6-1

K₁=0.2838 °K/mm Hg for metric units. =17.54 °Run, Hg for English units. 6.3 Saliur diands concentration.

Can =
$$K_2$$

$$\frac{(V_i - V_{ib}) \ N(\frac{V_{solo}}{V_s})}{V_{solock}}$$
Equation 6-2

Nere. K₁=22 m me/meq. for metric units. =7.051×10→ lb/meq. for English units.

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METHOD 7—DETERMINATION OF NITSOGEN OFFICE EMPHONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle A grab sample is collected in an every sted flask containing a dilute solitane acid-bydrogen peroxide absorbing solution, and the nitrogen endes, except nitrous oxide, are measured colorimsterically using the phenoidisulfonio-acid (PDB) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary nestranate of introduced and another two settlements to be 2 to 400 milligrams NO₂ (as NO₂) per dry standard cubic mater, without having to dilute the sample.

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 smincleast sample volume to allow analytical reproducibility to within ±5 percent, will be considered acceptable alternatives, rubber to approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

equipment is used in sampling:

2.11 Probe. Boroulicate glass imbing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a ping of glass wool is satisfactory for this purpose). Stainless steal or Tefon * tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

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

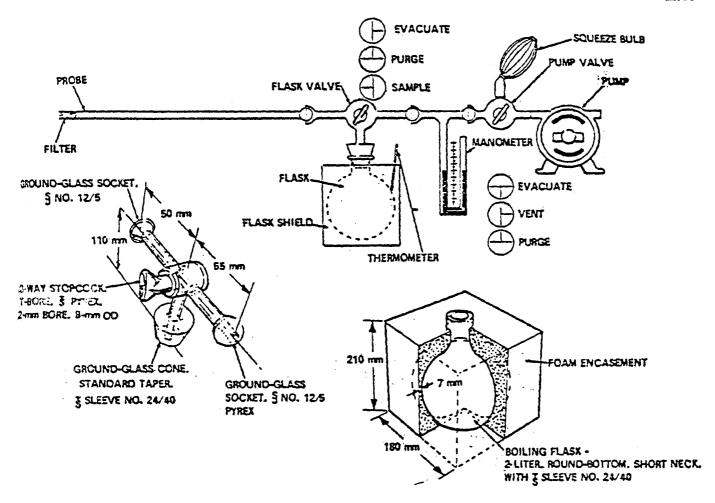


Figure 7-1. Sampling train, flask valve, and flask.

21.2 Collection Flank, Two-liter borosilicats, round bottom flank, with stort neck and 24/40 standard taper opening, protected against implusion or breakage.

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

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

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

21.5 Vaccum Osnes. U-tube manometer, 1 meter (36 in.), with 1-mm (0.1-in.) divisions, or other gauge expebte of measuring pressure to within ±2.5 mm Hg (0.10 in. 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.

2.1.7 Pump. Capable of evacuating the conscious fast 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 Stop-ock and Ground Joint Grease. A high-vacuum. high-temperature chlorofinocrocarbon grease is required. Halocarbon 25-53 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 barometris reading may be obteined from a nearby national weather seading may be obteined from a nearby national weather seation, 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 varia for elevation decrease.

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

2.1.1 Graduated Cylinder, 50 ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bortles.

22.3 Wash Bottle. Polyethylene or glass.
22.4 Glass Stirring Rod.
22.1 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

Analysis. For the analysis, the following equip-is needed: mentan

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

2.1.2 Porcaisin Bysporating Dishes, 175- to 250-mi capacity with lip for pouring, one for each sample and each standard. The Coors No. 45008 (shallow-form, 195 mi) has been found to be satisfactory. Alternatively, polymethyl pentene boakers (Naige No. 1203, 150 mi), or glass beakers (150 mi) 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).

2.1.3 Steam Bath Low-temperature overs or thermostatically controlled hot plates kept below 70° C (150° P) are acceptable siternatives.

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), 100 ml (one for each sample), 20.10 ml (one for each sample).

(one). 2.3.8 Spectrophotometer. To measure absorbance at

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.
2.3.9 Oradizated Pipetta. 10 ml with 0.1-ml divisions.
2.3.10 Text 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. Respents

3. Respenie

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 svailable grade.

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

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

imple 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 Diluga-74, Type 1 At the option of the

avalyst, the KMNO, test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

1.3 Analysis For the analysis, the following reasonts are required:

3.3.1 Furning Sulturic Acid. 13 to 13 percent by weight free sultur trioxide. HANDLE WITH CAUTION.

3.3.2 Sulture Acid. Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

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

3.3.5 Standard ENO, Solution. Dissolve exactly 2.198 g of dreed potassium nitrate (ENO₃) in desonated, distilled water and distuse to 1 liver with delonized, distilled water and distuse to 1 liver with delonized, distilled water in a 1,000-ml volumetric diak.

3.3.6 Working Standard ENO₃ Solution. Dilute 10 ml of the standard solution to 100 ml with desonized distilled water. One milliture of the working standard solution is equivalent to 100 ag nitrogen disade (NO₃).

3.3.7 Phenoidisullonic Acid Solution. Dissolve 25 g of pure white phenoi in 150 ml concentrated similaric acid on a steam bath. Cool, add 75 ml furning suituric acid on a steam bath. Cool, add 75 ml furning suituric acid, and heat at 100° C (212° F) for 2 hours. Store in a dark, stoppered bottle.

4. Procedures

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 supper into the flask with the valve in the "purgs" 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 greated with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock greate. Turn the flask rairs and the pump valve to their "evacuate" positions. Evacuature flasks to 75 mm Hg (3 in, Hg) absolute pressure, or less. Evacuation to a pressure approaching the valor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for lessage by observing the manometer for any pressure fluctuation. (Any variation

presier than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flack is not to be used until the leakage problem is corrected. Freesura in the mask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commanced.) Record the volume of the flack and valve (V), the disk temperature (Ti), and the barometric pressura. Turn the flack valve counterlockwise to its "purge" position and do the same with the pump valve. Purge the probe and the same with the pump valve. Purge the probe and the recurs in the probe and the risak valve area, best the probe and purse until the condensation disappears. Next, turn the pump valve to its "vents" position. Turn the flack valve clockwise to its "vents" position. Turn the flack valve clockwise to its "vents" position. Turn the flack valve clockwise to its "vents" position. Turn the flack valve clockwise to its "vents" position. Turn the flack valve clockwise in the mercury lavals in the manometer. The absolute internal pressure is the manometer reading. Immediately turn the flack valve to the "sample" position and permit the gas to enter the flack until pressures in the flack and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds: a longer pariod indicates a "ping" in the probe, which noust be corrected before sampling is continued. After prediction and disconnect the flack from the sampling trans. Shake the flack for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient errors for the convertion of NO to NO; (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mirrore of NO to NO; hall a sample of a calibration gas mirrore of NO to NO; thing the sample of the standard may require taking a sample of a calibration gas mirrore of NO to NO; thing the sample of the standard may require taking a sample of a calibration gas mirrore of NO to NO; thing the sample of the standard may require taking a sample of a calibration gas mirrore of NO to NO; thing th

erreen for the conversion of NO to NO; (e.g., an applicable subpart of the standard may require taking a sample of a culibration gas mixture of NO in Ne;), then orzers shall be introduced into the flack to permit this currerson. Oxygen may be introduced into the flack to the flack by cre of three methods; (I) Before evacuating the exampling flack, much with pure cylinder oxygen, then evacuate flack to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) inject oxygen into the flack after sampling; or (3) terminate empliing with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flack, record this flack pressure, and then yent the flack to the atmosphere until the flack pressure is almost equal to atmosphere intil the flack pressure is almost equal to

stmoorphoric pressure.

4.2 Sample Recovery Let the flask set for a minimum of 16 hours and then abake the contents for 2 minutes. Connect the flask to a mirroury filled U-cube manometer. Open the valve from the flask to the manometer and record the flask temperature (Tr), the barometric pressure, and the difference between the macroury levels in the manimater. The absolute internal pressure in the flask (Pr) is the barometric pressure less the manemater reading. Transfer the contains of the flask to a leak-tree polyechylene bottle. Plans the flask twice with 5-mi portions of demnized, dirulled water and add the rinse water to the borus. Adjust the pH to between 9 and 12 by adding sodium hydroxide (I N), drupwise 1 hours I to 25 to 25 forms). Cherk the nE by digning a (about 25 to 25 drops). Check the pR by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Ramove so little meatrial as possible during this step. Mark the bearnt of the liquid level so that the container can be charized for leakage after transport. Label the comment to clearly identify its contents. Seal the container for shipping.

that the container can be christed for leakage after transport. Label the container to clearly identify its contents. Seal 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 lest during and confirm whether or not any sample was lest during and confirm whether in on the analysical data sheet. If a noticeable amount of leakage has occurred, either void the Administrator, to correct the final results. Immediably prior to analysis, transfer the contents of the chipping container to a 30-ml volumetric flask, and mas the container twice with 6-ml portions of datonized, distilled water. Add the rinse water to the flask and dillute to the mark with delonized, distilled water, mix inhoroughly. Pipette a 25-ml aliquot into the processin eraporation dish. Resum 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 cook. Add 2 ml phenoidismilence and solution to the dried residue and triturate thoroughly with a poviethylene policeman. Make sure the solution contacts all the residue. Add 1 ml delonized, distilled water and four drops of concentrated sulfure acid. Heat the solution on a steam bath for 3 minutes with occasional surring. Allow the solution to cook add 20 ml delonized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwie, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by fitration (centrifugation is an acceptable alternative, subject to the acoptoval of the Administrator), as follows: fitter through whatman No. 41 filter paper into a 100-ml volumetric flash; num the evaporating dish with three form portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flash in the form worker, the solution can be transferred directly to the liter washings to the con

5.1 Finsk Volume. The volume of the collection finsk-fast: valve combination must be known prior to eximpling. 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.

3.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination. For both fixed and variable wavelength spectrophotometers, calibrate against standard certified wavelength of 410 mm, every 6 months. Alternatively, for variable wavelength spectrophotometers, scan the spectrum between 400 and 415 mm using a 200 sg NO 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 mm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of ab-

paired, when a pear 13 observed at which this peak occurs shall be the optimum wavelength for the measurement of absorbance for both the standards and samples. S.2.2 Determination of Spectrophotometer Calibration Pactor E. Add 0.0, 1.0, 2.0, 3.0, and 4.0 mi of the ENO, working standard solution (1 mi=100 ag NO) to a series of five porceiain evaporating dishes. To each, add 23 mi of absorbing solution, 10 mi desonized, distilled water, and sodium hydroxide (1N), dropwise, until the water, and sodium hydroxide (IN), dropwiss, until the pH is between 9 and 12 (shout 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.2, until the solution has been transferred to the 100 ml volumetric flask and diffused 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:

$$K_{s} = 100 \frac{A_{1} + 2A_{2} + 3A_{1} + 4A_{4}}{A_{1}^{2} + A_{2}^{2} + A_{1}^{2} + A_{1}^{2}}$$

Equation 7-1

4 Temperature Gauge, Calibrate dial thermometers

against mercury-ingiass thermometers.
5.5 Vacuum Gauge. Calibrate mechanical cauges, if used, against a mercury manameter such as that speci-

tied, against a mercury manameter such as that speci-fied in 2.1.5.
5.5 Analytical Balance. Calibrate against standard weights.

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figure after final calculations. 6.1 Nomenclature.

A = Absorbance of sample.
C=Concentration of NO: as NO:, dry basis, corrected to standard conditions, mg.dscm

C=Concentration of NO: as NO: ary base, or recited to standard conditions, mg deem (lb/decf).

P=Diffusion factor (i.e., 25/3, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_{*}=Spectrophotometer calibration factor.

m=Hass of NO: as NO: in gas sample, sf.

P_{*}=Final absolute pressure of flask, mm Hg (in. Hg).

Hg. lnittle absolute pressure of flask, mm Hg (in. Hg).

Hg).

P_{***}=8 tandard absolute pressure, 760 mm Hg (20.72 in. Hg).

T_{*}=8 tandard absolute pressure of flask, *K (*R).

T_{*}=1 initial absolute temperature of flask, *K (*R).

T_{**}=8 tandard absolute temperature, 25° K (528° R).

V_{**}=8 ample volume at standard conditions (dry basis), ml.

V_{*}=Volume of flask and valve, ml.

V_{*}=Volume of flask and valve, ml.

2 50725, the slingost factor. (If other than a 25-ml slingost was used for analysis, the corresponding factor must be substituted).

8.2 Sample volume, dry basis, corrected to standard orditions.

 $\begin{aligned} V_{*i} = & \frac{T_{*id}}{P_{*id}} \left(V_f - V_{*} \right) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \\ = & K_i \left(V_f - 25 \text{ ml} \right) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \end{aligned}$

Equation 7-2

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

=17.64 oR for English units

6.3 Total ag NO: per sample.

 $m=2K_cAF$

Equation 7-3

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

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

$$C = K_2 \frac{m}{V_{44}}$$

Equation 7-4

where:

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

=6.243×10 $\rightarrow \frac{\text{lb/scf}}{\mu g/\text{ml}}$ for English units

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METHOD S-DETERMINATION OF SULFURIC ACM MINE AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle one apparenting
1.1 Principle. A gas sample is estracted isokinetically
from the stack. The sulture acid mist (including sultur
trioxide) and the rultur dioxide are separated, and both
fractions are measured separately by the barnum-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/emble detectable limits of the method are 0.05 milligrams/onble meter (0.05):10-7 pounds/emble foot) for suitur trioxide and 1.2 mg/m² (0.74 10-7 lb/ft) for suitur trioxide and 1.2 mg/m² (0.74 10-7 lb/ft) for suitur dioxide. No upper limits have been established. Based on theoretical calculations for 200 millilitars of 3 persont bydrogen peroxide solution, the upper concentration limit for suitur dioxide in a 1.0 m² (35.3 ft) gas sample is about 12,500 mg/m² (7.7×10-4 lb/ft). The upper limit can be extended by increasing the quantity of peroxide solution to the impagement in the impingers.

Possible interfering agents of this method are finorides, 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 SO₃ and SO₂ (subject to the approval of the Administrator); however, the procedure used for particulate matter must be consistent with the specifications and procedure given in Method 5.

2. Appendius

21 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 one-struction 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. subsections.

The operating and maintenance procedures for the sampling train are described in APTD-657d. Since correct usage is important in obtaining valid results, all uses about read the APTD-657d 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 to a 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

21.2 Probe Liner. Borodileate or quartz give, with a beautig system to prevent visible condensation during sampling. Do not use metal probe liners.

21.2 Pitot Tube. Same as Method 5, Section 21.3.

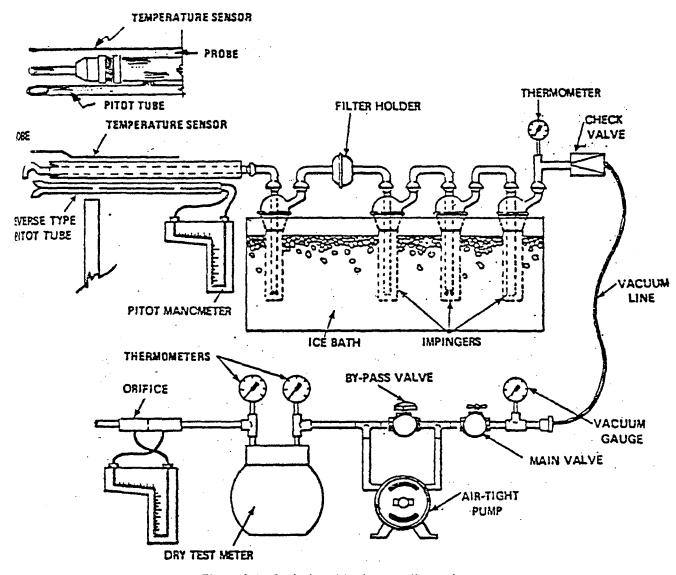


Figure 8-1: Sulfuric acid mist sampling train.

[4] Differential Pressure Gauge, Same as Method 5,

ii) Differential Pressure Gauge.

13) Filter Holder. Borosilicate glass, with a glass filter support and a alloone rubber gastet. Other amaterials, e.g., Teslon or Viton, may be used sub-ii the approval of the Administrator. The holder parallel portide a positive seal against leakage from Sixile or around the filter. The filter holder shall beed between the first and second impingers. Note:

ised between the first and second impingers. Note: not best the filter hoider.

16 Impingers—Four, as shown in Figure 8-1. The und third shall be of the Greenburg-Smith design itsandard tips. The second and fourth shall be of Greenburg-Smith design, modified by replacing the fighth an approximately 13 millimeter (0.5 in.) ID flube, having an unconstricted tip located 13 mm [h] from the bottom of the fisak. Similar collection and, which have been approved by the Administration be used.

Metering System. Same as Method 5, Section

of may be used.

Metering Sy

Barometer.

Gas Density Barometer, Same as Mathed 5, Section 2.1.9.

13) Gas Density Determination Equipment. Same (sibe) 5. Section 2.1.10. (1) Temperature Cauge. Thermometer, or equivatio measure the temperature of the gas leaving the differentian to within 1° C (2° F). libample Recovery.
11 Wash Bottles. Polyethylens or glass, 500 ml.

27 Ordinated Cylinders, 250 mt, 1 liter, (Volu-no flacks may also be used.) 23 Storace Bottles, Leak-line polyethylens bottles,

mi size (two for each sampling run).

2.2.4 Trip Balance. 500-gram capacity, to measure to ±0.3 g (necessary only if a moisture content analysis is to be done).
2.3 Analysis.
2.3.1 Pipettes. Volumetric 25 ml, 100 ml.

2.3.1 Pipettes. Volumetric 25 ml, 100 ml.
2.3.2 Burrette. 50 ml.
2.3.3 Erlenmeyer Flask. 250 ml. (one for each sample

2.3.3 Erienmeyer Plack. 20 ml. (one for each sample blank and standard).
2.2.4 -Oraduated 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 Respents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

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. Delonized, distribed to conform to ASTM specification Dil93-74. Type 3. At the option of the analyst, the KMnO; test for orditable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.4 Lappropanol. 80 Percent. Mix 800 ml of isopropanol with 200 ml of delonized, citutiled water.

NOTE—Experience has shown that only A C S. grade.

Note.—Experience has shown that only A.C.S. grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commercial sources occasionally has persited impunities that will cause excessionally has persited impunities that will cause ex-

reneously high sulfuric sold mist measurement. Use the following test for detecting peroxides in each lot of isopropenol: Shake 10 ml of the isopropenol with 10 ml the following test for detecting permides in each lot of isopropanol: Shake 10 mi of the isopropanol: with 10 mi of freship prepared 10 percent potassium folide solution. Prepare a blank by similarly treating 10 mi of distilled water. After I minute, read the absorbance on a spectrophotometer at 332 nanometers. If the absorbance exceeds 11. the isopropanol shall not be used. Percuides may be removed from isopropanol by redistilling, or by passage through a column of activated alumina. However, reagant-grade/isopropanol with suitably low percuide/levals is readily awaisable from commercial sources, therefore, rejection of contaminated lots may be more smiciant than following the percuide removal procedure.

3.1.5 Hydrogen Percuide, 3 Percent. Dilute 100 mi of 30 percent bydrogen percuide to 1 liter with deionized, distilled water. Prepare fresh daily.

3.2.1 Esympaeuol, 80 Percent. Same as 3.1.4.

3.2.2 Esympaeuol, 80 Percent. Same as 3.1.4.

3.3.1 Water. Same as 3.1.2.

3.3.2 Hopmopaool, 100 Percent.

3.3.3 Thorn Indicator. 1-(o-aronophenylazo)-2-capholic, 6-distillonic acid, disodium sait, or equivalent. Disolve 0.09 gin 100 mi of deionized, distilled water.

3.3.4 Barium Perchiorate (n.0100 Normal). Disolve 1.85 go foarium perchiorate, turbydrate (BaCCheller) in 200 ml deionized, distilled water, and dilute to 1 liter with insproanol; 1.22 g of barium chloride dishydrate (BaCCheller) may be used instead of the barium perchiorate. Standardium with sulture acid as in Section 5.2. This solution must be protected against evaporation as all times.

2.25 Sulfurie Acid Standard (2.000 N). Purchase or standardize to mc10002 N sening 0.0100 N NeOH that has previously been standardized against primary standard potassium acid phthalasa.

4. Procedure

4.1 Sampling.

4.1 Sampling.
4.1.1 Prairies Preparation. Follow the procedure outlined in Method 5, Section 4.1.1; filters should be inspecied, but need not be desicosted, weighed, or identified. If the similar gain 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 (steeps for the second paratraph and other obviously inapplicable parts) and use Figure 8-1 instead of Figure 5-1. Replace inc. second paratraph with: Place 100 ml of 80 persons isopropanol in the first impurger, 100 ml of 3 persons hydrogen paratids in both the second and third im-

pingers: retain a portion of each reagent for use as a blank solution. Place about 200 g of since gel in the fourth hansper.

Impurger. If moisture content is to be determined by impinger analysis, weight each of the first three impingers (plus absorbing saintion) to the nearest 0.5 g and record these weights. The weight of the silics sel (or silics get plus container) must also be determined to the nearest 0.5 g and recorded.

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Date shall be recorded

on a sheet similar to the one in Figure 8-2. The sampling rate shall not encest 0.000 m/min (1.0 cfm) during the rim. Periodically during the test, observe the connecting line between the probe and first impacter for some of condensation. If it does occur, adjust the probe beater setting unward to the minimum tamperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done im-mediately before each change, according to the procedure outlined in Section 4.1.4.2 of Mathod 5 (with appropriate modifications, as mentioned in Section 414 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 med.

PLANT						STATIC PRESSUR	· ·			
LOCATION					1	RESSURE				
DPERATOR					l	PROBE LENGTH, m (ft)				
DATE					j					
RUN NO					1					
Sample box nd. 🗀					1	AVERAGE CALI	BRATED NOZZ	LE DIAMETER,	em (ia.)	
METER BOX NO					į	PROBE HEATER	SETTING			
GH A RETEM			LEAK RATE, m3/min,(cfm)							
C FACTOR			PROBE LINER MATERIAL							
PITOT TUBE COEFF	icient, c _p		SCHEMATIC OF STACK CROSS SECTION FILTER NO.							
_			VELOCITY DIFFERENTI ACROSS STACK HEAD ORIFICE		ORIFICE		GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING	
TRAVERSE POINT NUMBER	SAMPLING TIME (0), mis.	MACUUM mm Hg (in, Hg)	TEMPERATURE (Ts), °C (°F)	mm H20 (in. H20)	METER, mm H20 (in. H20)	GAS SAMPLE VOLUME, m3 (t/3)	· INLET, °C (°F)	OUTLET, °C (°F)	CONDENSER OR LAST IMPINGER, °C (°F)	
	,									
									·	
			•							
							,			
		•								
				·						
					1					
								-		
				1		1	·			
TOTAL							Avg	Avg		
AVERAGE							Avg			

Figure 8-2. Field data.

After turning off the nump and recording the final After turning off the pump and recording the final roddings at the conclusion of each run, rumove 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 cultier 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 proba disconnected, pourse the remaining port of the train, by drawing clean applicut air through the system for 15 minutes at the average flow rate used for sampling.

Note:—Clean are highest one he provided by possing

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

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

4.2 Sample Herovery.

4.21 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 200-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 30 percent isopropanel. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanel. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution

and transfer to the storage container. Protect the solution against evaporation. Nark the level of liquid on het container and identify the sample container.

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

Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. Runse all connecting glassware including back half of filter holder) between the filter and silica gel impinger with desonized,

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

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

4.3 Analysis.

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

4.3.1 Container No. 1. Shoke the container holding the isopropanol solution and the filter. If the filter breaks up, slick whe fragments to settle for a few minutes before removing a sample. Pir-sete a 100-mi dispost of this solution into a 200-mi Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and tirste to a pink and pelintusing 0.0190 N barium perchlorate. Repress 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.
4.1.2 Container No. 2. Thoroughly mix the solution in the container holding the containts of the second and third implingars. Pipetre a 10-ml aliquot of sample into a 250-ml Erisameyer flask. Add ml of isopropanol. 2 to 4 drops of thorn indicator, and titrate to a pink end point using 0.0100 N berium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate directions must agree within 1 percent with a second alliquot of sample and average the titration valuas. Replicate directions must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.3 Blanks. Prepare blanks by adding 2 to 4 drope of thorin indicator to 100 mi of 80 percent isopropenol. Titrate the blanks in the same manner as the samples.

S.I. Calibrate equipment using the procedures specified in the following sections of Mathod 5: Section S.3 (metering system); Section S.5 (temperature gauges); Section S.7 (baromater). Note that the recommended leak-check of the metering system, described in Section S.6 of Mathod S. also applies to this method.

S.2 Standardise the barium perchlorate solution with 25 ml of standard soliturie acid, to which 100 ml of 100 percent isopropenced has been added.

Note.—Carry out calculations retaining at least one extra decimal frume beyond that of the sequired data. Bound off figures after final calculation. 6.1 Nomenclature.

6.1 Nomenciastre.

A.=Cross-sectional area of nostla, m³ (fif).

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

CH:60.=Bullurie acid (including 80) concentration.

g/dscm (b)/dscf).
CSO:=Sulfer dioxide concentration, g/dscm (b/

Improvement of isokinatic mampling.

N=Normality of barium perchlorate titrant, grequivalents/liter.

Phar-Barometrio pressure at the sampling site, mm Hg (ln. Hg).

P.-Absolute stack gas pressure, mm Hg (ln.

P.=Absolute stack gas pressurs, mm Hg (in. Hg).

Pstd=8tandard absolute pressurs, 700 mm Hg (20.92 in. Hg).

T=-Average absolute dry gas meter temperature (see Figure 8-2), * K (* R).

T=Average absolute stack gas temperature (see Figure 8-2), * K (* R).

Total standard absolute temperature, 200° K (200° R).

V=Volume of sample aliquot titrated, 100 ml (or E80c and 10 ml for 80c.

Vi=Total volume of the did of the 80c.

Vi=Total volume of the sample as measured by dry gas meter, dem (def).

V=(std) = Volume of gas sample as measured by the dry gas meter corrected to mandard conditions, dem (def).

Jerges stack gas velocity, calculated by sample as meters of the sample measured by dem (def).

Jerges stack gas velocity, calculated by sample as meters.

daem (daef).

**Average stack gas velocity, calculated by Method 2. Equamom 2-9, using data obtained from Method 8, m/sec (tt/sec).

*Visin=Total volume of solution in which the sulturic solid or sultur dioxide sample is contained, 250 mi or 1,000 ml, respectively.

*Vi=Volume of bardium perchlorate fitrant used for the sample, ml.

*Vi=Volume of bardium perchlorate fitrant used for the blank, ml.

Vin = Volume of barium perchlorate titrant used for the black, mi.
Y= Dry gas meter calibration factor.
AH=Average pressure drop across orifice meter, mm (in.) HrO.
8 = Total sampling time, min.
13.5 = Specific gravity of mercury.
60 = sec/min.
100 = Conversion to percent.
5.2 Average dry gas meter tamperature and average critice pressure drop. See data sheet (Figure 8-2).
6.3 Dry Gras Volume. Correct the sample volume measured by the dry gas meter to standard conditions (CO C and 760 mm Hg or 65° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{\text{m (and)}} = V_{\text{m}} Y \left(\frac{T_{\text{aid}}}{T_{\text{m}}} \right) \frac{P_{\text{bar}} + \left(\frac{\Delta H}{13.6} \right)}{P_{\text{and}}}$$

$$=K_1V_mY\frac{P_{bar}+(\Delta H/13.6)}{T_m}$$

Equation 8-1

where:

K_= 0.3338 * K/mm Hg for metric units.

=17.64 * R/in. Hg for English units.

Nove.—If the leak rate observed during any mandatory irak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_e in Equation 8-1 as described in Section 6.3 of Method 5), or shall invalidate the lost 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 implicates 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 6-3 of Method 5 also applies to this method. Note that if the efficient gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Solium as all mix fixed inciding 80.0 concentration.

6.5 Sulfuria acid mist (including 80) concentration.

$$C_{\rm H_2 6O_4} \!=\! K_3 \frac{N(V_i \!-\! V_{\rm tb}) \left(\frac{V_{\rm soln}}{V_a}\right)}{V_{\rm m \, (cud)}}$$

Equation 8-2

ners:
Li=0.04904 g/milliequivalent for matric units.
=1.081×10=16/meq for English units.
6.6 Builtre dioxide concentration.

$$C_{SO_2} = K_2 \frac{N(V_t - V_{tb}) \left(\frac{V_{tota}}{V_a}\right)}{V_{total}}$$

Equation 8-3

E = 0.0200 g/moq for metric units. = 7.061 × 10 → 10/moq for English units. 6.7 Isokuetic Variation. 6.7.1 Calculation from raw data.

$$I = \frac{100 T_{\bullet} [K_{\bullet} V_{(\bullet} + (V_{\bullet}/T_{\bullet}) P_{bar} + \Delta H/13.6)]}{60 \theta V_{\bullet} P_{\bullet} A_{\pi}}$$

Equation 8-4

where:

K:=0.003484 mm Hg-m³/ml-°K for metric units.

=0.002878 in. Hg-tt/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_{\circ}V_{m (sud)}P_{sid} 100}{T_{sud}v_{\circ}\theta A_{o}P_{\circ}60 (1-B_{vo})}$$
$$= K_{\delta} \frac{T_{\circ}V_{m (sud)}}{P_{\circ}v_{o}A_{o}\theta (1-B_{vo})}$$

Equation 8-5

where: $K_1=4.200$ for metric units. =0.09450 for English units. 6.8 Acceptable Results. If 90 percent $\le 1 \le 110$ 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 Mathod 5 to make judyments. Otherwise, reject the results and repeat the test.

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(Secs. 11, 114, 301(a), Clean Air Act, sec. 4(a) of Pub. L. 91-604, 94 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. 1357c-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, heart it into the stack, and sample at a constant rate of $2 \text{ lpm} (0.07; \pm m)$. Costume sampling until the dry sas meter restricts about 30 liters (1.1 ft?) or until visible highed droplets are carried over from the first immingst to the second, Record temperature, pressure, and dry gas meter readings as required by Figure 4-3.

required by Figure 4-1.

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

3.2 Calculations. The calculation method presented is

3.3 Calculations. The calculation method presented is designed to estimate the mossure in the stack fast 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 lacking the moisture plung rate settings.

B... Approximate: proportion, by volume, of water vapor in the gas stream leaving the second improses 0.075.

B... Water vapor in the gas stream, proportion by volume.

wolume.

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

P=Absolute pressure for this method, same as barometric pressure, is the dry gas meter.

P=id=Standard absolute pressure, 760 mm Hg
(29.32 in. Hg)r=i=

R=ideal gas constant, 0.08236 (mm Hg) (mf)/(g-mole) (%) for metre units and 21.85 (in. Hg) (hf)/lb-mose) (*R) for English units.

(in. Hg) (BP)(b-moss) (*R) for English units.

T==Absolute temperature at meter. *K (*R)

T==Standard absolute temperature, 233° K (528° B.)

V.= Final volume of impinger contents, ml.
V.= Linital volume of impinger contents, ml.
V.= Dry gas volume measured by dry gas mater,
dem (def)

 $V_{m(old)}$ =Dry gas volume measured by dry gas meter, corrected to granderd conditions, decre

(deef).

Volume of water vapor condensed, corrected to standard conditions. scm (scf).

Density of water, 0.982 g/ml (0.00201 lb/ml).

3.3.2 Volume of water vapor collected.

$$\begin{split} V_{\text{un}} = & \frac{(V_f - V_i)_{\theta = RT, \text{tot}}}{P_{\text{out}} M_{\text{u}}} \\ = & K_1^- (V_f - V_i) \end{split}$$

Equation 4-5

K₁=0.001333 m4/ml for metric units =0.04707 ft²/ml for English units

2.3.3 Gas volume:

$$V_{m} \left(\frac{P_{m}}{P_{m,i}} \right) \left(\frac{T_{m,i}}{T_{m}} \right)$$

$$= K_{1} \frac{V_{m} P_{m}}{T_{m}}$$

Equation 4-6

where: ners: K:=0.386 °K/mm Hg for metric units =17.64 °R/m. Hg for English units 3.24 Approximate moisture content.

$$B_{ro} = \frac{V_{we}}{V_{we} + V_{m \text{ (sed)}}} + B_{max}$$

$$= \frac{V_{we}}{V_{we} + V_{m \text{ (sed)}}} + \frac{\tau}{(0.025)}$$
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 (becometer). The recommended leak check of the metering system (Section 5.6 of Method 5) check of the metering system (Section 5.5 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.

8. Bibliography

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2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeies, Calif. November, 1983.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of 159 Manufacturing Co., Los Angeles, Calif. Bulletin WP-50, 1988.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS
FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isorkinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 120±14° C (248±23° F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator, U.S. Environmental Protection Ageory, for a particular application. The particulars mass, which includes any material that condenses at or shove the fibration temperature, is determined gravimetrically after removal of uncombined

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

2. Apperatus

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-0881 (Citation 2 in Section 2); commercial models of this train are also available. For changes from APTD-0881 and for allowable modifications of the train shown in Figure 5-1, see the following subsections:

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 berein. The sampling train consists of the following components:

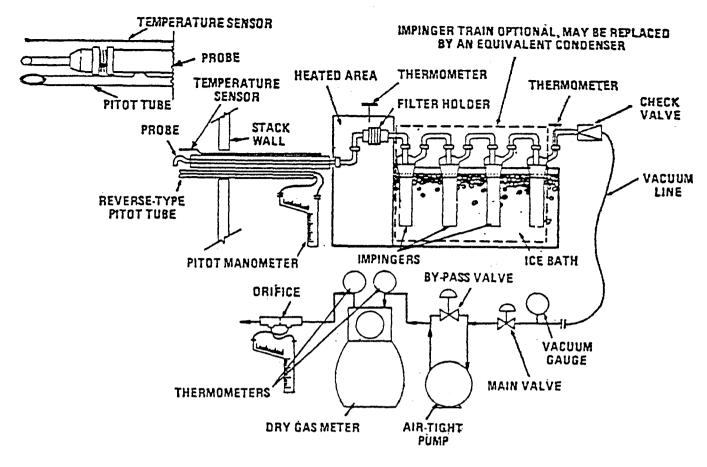


Figure 5 1. Particulate-sampling train.

2.1.1 Probe North. Stabaless steel (216) or gless with sharp, tapered leading edge. The angle of taper shall be \$20° and the taper small be at the outside to preserve a constant teaternal diameter. The proble mostle shall be of the button-book or elbew design, unless otherwise specified by the Administrator. If made of stabless steel, the nortie shall be constructed from samiless sub-ing other materials of construction may be used, subject to the approval of the Administrator.

A range of nowtle mass suitable for isokinetic sampling should be available, a.g. 0.22 to 1.27 cm (1/4 to 1/4 fm.)—or larger if higher volume sampling trains are used—inside diameter (1D) nowless in increments of 0.16 cm (1/8 to 1/2 Probe Liner. Borosilicate or quarts glass rubing with a beating system capable of maintaining a gas temperature at the satt end during sampling of 120±14° C (216±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 at the outlet of the probe is not usually monitored during sampling, probas constructed according to APTD-0.881 and utilizing the calibration curves of APTD-0.882 and utilizing the calibration curves of APTD-0.882 and utilizing the calibrat

Mention o trade names or specific product: does not intitute endorsement by the Environmental Protocc nstitute er

plane of the pitot tube shall be even with or above the nonlie unity plane (see Method 2, Figure 2-6b) during sampling. The Type 8 pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differentia. Pressure Gauge. Inclined manoruser or equivalent deven (two), as decribed in Section 2.2 of Method 2.0 ne manameter shall be used or velocity, beed (ap) readings, and the other, or ordice differential pressure readings.

pressure readings.

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

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 o. 120±14° C (248±2° 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 modifored during sampling. Heating systems other than the one shown in APTD—0381 may be used.

2.1.7 Condenser. The following system shall 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-iree ground glass littings or any similar less-lice non-contaminating fittings. The first, third, and fourth impingers shall be or the Greenburg-Smith desum, modified by reclacing the tip with 1.3 cm (1/4 in.) ID glass tube extending to about 1.3 cm (1/4 in.) If om the bottom or the flask. The second impinger shall be or the Greenburg-Smith design with the standard (ip. Modifications (e.g., using flexible connections between the impingers, using materials other than class, or using flexible racum 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 stuch get, or equivalent desiceant. A thermometer, capable of measure Condenser. The following system shall be used

ing temperature to within 1° C (2° F) shall be placed at the outlet of the fourth impinger for monitoring

proces.
Alternatively, any system that cools the sample gas Alternatively, any system that cools the sample gas stream and allows measurement of the water coodensed and moisture leaving the condenser, such to within 1 mi 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 coodenser by:

(I) monitoring the temperature and pressure at the exit of the condenser and using Dailon's taw of partial pressures; or (2) passing the sample gas stream through a tured silica gel (or equivalent desiceant) tray with exit gases kept below 20° C (65° 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 second-need 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.

Notz.—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, individua. States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger outents.

2.1.3 Metring System. Vacuum gauge, leak-free

the absolute barometric pressure) shall be requested and an adjustment for also and differences between the weather station and sampling point small be applied at a rate of minus 2.5 mm Hg (6.1 m. Hg) per 30 m (100 to disvation increase or vice versa for elevation decrease, -2.1.10 Gas Dannty Determination Equipment. Temperature sensor and pressure gause, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 2. 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 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 5 pitot tube openings (see Method 2, Figure 2-7). As a second aircrimative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature rause 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 Itams are needed.

needed.

needed.

2.2.1 Probe-Liner and Probe-Nozzle Brusbes. Nylon brustle brusbes with stainless steel wire handles. The probe brush shall have extensions iat least as long as the probe of stainless steel, Nylon, Teston, or similarly inert material. The brusbes shall be properly sized and shanold to brush out the probe liner and nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended, polysthylene wash bottles may be used at the option of the tester. It is recommended that acctone not be stored in polysthylene bottles for longer than a month. Proba-Lines and Proba-Norsia Brosbas, Nylon

month.

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

2.2.4 Petri Dishes. For filter samples, glass or polethylene, unless otherwise specified by the Admin-

ethylene, unless otherwise specified by the Administrator.

2.2.5 Oraquisted Cylinder and/or Balanca. To messure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. blost 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 silicagel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica sel to container; not necessary if silica

transfer of stilics get to container; not necessary if silica get is weighed in the field.

2.2.8 Funnei. Glass or polyethiems, to aid in sample

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

2.3.1 Glass Weighing Disbes. 2.3.2 Desiccator.

Analytical Balance. To measure to within 0.3

mg.
2.3.4 Baianos. To measure to within 0.5 g.
2.3.5 Beakers. 250 ml.
2.3.6 Hygrometer. To measure the relative lumidity of the laboratory environment.
2.3.7 Temperature Gauge. To measure the tempera-

turn of the laboratory environment

3. Reosents

3.1 Sampling. The reagents used in sampling are as

follows:
3.1.1 Filters. Olars fiber filters, without organic 3.1.1 Filters. Olars fiber filters, without orranic binder, exhibiting at least 99.95 percent efficiency (\$0.05 percent penciration) on 0.3-micron diocyt phtholate moke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D. 265-71. 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 (330° F) for 2 hours. New silica gel may be used a received. Alternatively, other types of desicones (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 impinivers is required, distilled water shall be used. Kut hanks prior to hald use to climinate a high blank on teat samples.

on trac samples.

Crushed Ice.

3.1.4 Crished Ice.
3.1.5 Stopcock Gresse. Acctone-insoluble, heat-stable silrone gresse. This is not necessary if screw-on connecture with Teflon sleeves, or similar, are used. Alternatively, ther types of stopcock gresse may be used, subject to the approval of the Administrator.
3.2 Faminia Recovery, Acctone—resgent grade. ≤0.001 percent resulte, in glass bottles—is required. Acctone from metal containers generally has a high residue blank and should not be used. Sometimes, appliers transfer acctone to glass bottles from metal containers; thus, acctone thinks shall be run prior to field use and only acctone with low blank values (≤0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 metal to the weight of the whole of the subtracted from the stable of the subtracted from the section of the weight of feetone used be subtracted from ment of the weight of motions used he subtracted from

3.3 Analysis. Two reagents are required for the analy-

as:

13.1 Acesone, Same as 1.2

3.2.2 Desicoant, Anhydrous calcium sulfate, indicating type. Ajternatively, other types of desiceants may be used, subject to the approval of the Administrator.

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 sinca gel plus container, on each container. As an alternative, the silica gel need not be praweighed, 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 punhole leaks. Label filters of the proper diameter on the back ade 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

containers at all times except during sampling and weighing.
Desiceate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 28 hours and weigh at instervals of at least 6 hours to a constant weight, i.a., <0.3 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 streater than 2 minutes and a relative himmidity above 50 percent. Alternatively (galess otherwise specified by the Administrator), the filters may be oven dried at 105° C (20° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative himmidity 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, temporature, 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 isoxinetic sampling rate settings. Determine the stack as dry moiecular 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 rank , and for the same total length of time as, the perficulate sample run.

Select a nozzle size based on the range of velocity heads,

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

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 pius one-

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 swoid 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 its about to begin. Place 100 mil of water in each of the first two impingers, leave the third impinger amore, and transfer anomalies.

Place 100 ml of water in each of the first two impingers, leave the third impinger ampty, and transfer approximately 200 to 300 g of preweighed silica gol 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 ampling. Place the container in a cient place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.3 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed litter in the illiter holder. Be sure that the filter is properly centered and the gasket properly based so as to prevent the

and the gasket properly placed so as to prevent the sample gas stream from curcumventing 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 20° C (20° F) and an ashested string gasket when temperatures are higher. See APTD-6676 for

details. Other connecting systems using either 316 stain less steel or Tenon terrales may be used. When metal liners are used, install the nozzie as above or by a leakfree direct mechanical connection. Mark the probe with heat resistant tase or by same other method to denote the proper distance into the stack or duct for each sampling point

pung point.

Set up the train as in Figure 5-1, using (if necessary)
a very light cost of silicone greate 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 holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the SLECK COL

stark 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 recommended, our not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

Aftenthe sampling train has been assembled, turn on and set the filter and probe heating systems at the deured operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connections. tion is used in assembling the probe nords to the probe liner, leak-check the train at the sampling site by plug-ging the nottle and pulling a 380 mm Hg (15 in. Hg) TATILITY

NOTE.-A lower vacuum may be used, provided that

vacuum.

NoTE.—A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestoe string is used, do not connect the probe to the train during the leak-check, instead, leak-check to the train by first plurging the inlet to the thar holder (cyclone, if applicable) and pulling a 180 mm Hg (18 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 (18 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00037 m³,min (0.002 clm), whichever is less, are macceptable.

The following leak-check instructions for the sampling train described in APTD-656 and APTD-681 may be helpful; Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially apen the coarse adjust valve and slowly closed the bypass valve with 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 and 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 inunediately turn off the vacuum pump. This prevents the water in the implication of the plug form the inlet to the probe filter holder, and slice gel from being entrained backward into the filter holder and slice gel from being entrained backward into the third impinger.

silica gel from being entrained backward into the third

suica gei ironi oring samula Run. II. during impinger.

4.1.4.2 Leak-Checks During Sample Run. II. during the sampling run, a component (e.g., filter assambly 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 brocedure outlined in cection 3.1.11 should be tone as a vacuum equal to orgreater 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 minin (0.02 c(m) 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 slowen 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-Checks. 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 0.0037 m²/min (0.02 cm) or 4 percent of the average samplifier rate (whichever is less), the results are acceptable, and morrection need be applied to the total volume of dry ras metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate is not correct the sumple volume as shown in Section 6.36 this method,

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.

4.1.3 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 (283±25° F), or such other temperature as specified by an applicable subpart of the standards or approach by the Administrator.

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 such leak check, and when sampling is halted.

the other readings required by Figure 5-2 at least once is she sample point during each time increment and fittonal readings when significant changes (20 percent aution in velocity head readings) necessiate additional significants in flow rate. Level and tero the importance. Because the manomater level and zero may will due to vibrations and temperature changes, make

Clean the portholes prior to the test run to minimise the chance of sampling deposited metarial. To begat sampling, remove the nozzie cap, verily that the filter and probe heating systems are up to temperature, and that the pilot rube and probe are properly positioned. Position the nozzie at the first traverse point with the dip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which sid in the rapid adjust-

ment of the isokinetic sampling rate without ment of the lookinstic sampling rate without exceeding computations. These comparations are designed for use when the Type 8 pitot tribe conflicient is 10.53—2.00% and the stack gas equi-releast density (day molecular weight) is squal to 125—4. APT D=0.578 datasis the procedure for tring the nomographs. If C₅ and M_d are outside the above stated ranges do not use the homographs unless appropriate stops (see Citation 7 in Section 7) are taken to compensate for the deviations.

ZIANT	<u> </u>					7	AMBIENT TEM	ERATURE		
LOCATION			1				BAROMETRIC I	PRESSURE		
OPERATOR			1			1	HOM GEMUZZA	STURE, %	·	
DATE						1	ASSUMED MOISTURE, %			
RUN NO.			1				NOZZLE IDENI	REPORTABLE		
SAMPLE BOX NO			İ							m[i=1]
Meter box no										
Meter dhe			1				•			
CFACTOR			SCHEMA	TIC OF STAC	X CROSS SECTIO					
PITOT TUBE COEFFI	CIENT, C,					•				
					•		FILTER NO.			
	SAMPLING	VACUUM	STACK TEMPERATURE	VELOCITY HEAD	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER	Gas sample		Temperature Bas meter	EILTER HOLDER	TEMPERATURE OF GAS LEAVING CONDENSER OR
TRAVERSE POINT NUMBER	TIME (8), min.	mm Hg (in. Hg)	(Tg) •୯ (•ਸ)	(APs). num(in.)H ₂ Q	mm H ₂ O (in. H ₂ O)	VOLUME	INLES	OUTLS? *C (*f)	TEMPERATURE.	LAST IMPINGER, °C (°F)

				<u> </u>			 	·		
							 			
									-	
			•			^		1		·
-			1						<u> </u>	
TOTAL	1					<u> </u>	Avg.	Avg.		
AVERAGE		<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	Avg.		<u> </u>	

- Figure 5-2. Particulate field data.

When the stack is under significant negative pressure (height of impinger stem), text cars to close the coarse adjust wa're before inserting the probe into the stack to privent water from backing into the filter holder. If newstary, 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.

Therefore the stack presuments as required by Method

around the probe and porthole to prevent unrepresentative dilition of the mas stream.

Traverse the stack cross-section, as required by Method
for as specified by the Administratur, being careful not
being the probe noticle into the stack walls when
sampling near the walls or when removing or inserting
file probe through the portholest this minimizes the
chance of extracting deposited material.

During the test run, make periodic adjustments to
keep the "emperature around the filter holder at the
proper level; add more ire and, if necessary, salt to
condenser/siling gci outlet. Also, periodically check
the level and zero of the manumeter.

If the pressure drop across the filter becomes too high
making isolizatic sampling difficult to maintain, the
filter may be replaced in the midst of a sample run. It
is recommended that another complete filter assembly
is intel rather than attempting to change the filter itself.

Refore a new filter assembly is installed, conduct a leakcheck (see Section 41-4.2). The total particulate weight
shall include the summation of all filter assembly cauches.

A single train shall be used for the entire sampling in required

A single train some be used for the entire sample run, except in cases where simultaneous sampling is required in two or more different but one within the same duct, or, in cases where equipment-follows one within the same duct, or, in cases where equipment-follows necesstates a change of trains. In all other situations, the size of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate Note that when two or more trains are used, separate analyses of the Iron-half and (II applicable) impinger catches from each train shall be performed, unless identical nozile 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 iron-half catch and one analysis of iron-half catch and one analysis of iron-half catch and one analysis of details concerning the calculation of results when two or details concerning the calculation of results when two or more trains are used.

more trains are used.

At the end of the cample run, turn off the coarse adjust valve, remove the probe and nozule from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-tast leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3 in the lines must reas 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.

rates.

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 notificand places can over it to prevent losing or gaining particulate matter. Do not cap off the probe tip lightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impurgers into the filter holder.

Before moving the sample train to the cleanup size, remove the probe from the sample train, with our the

silicone crease, 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 instead and cap it. Remove the unbilical cord from the last impinger and can the impinger of feetble 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 of the visione 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 openitors. Transfer the probe and filter-impinger assembly to the cleanup area. This area should be crean and protected from the wind so that the chances of contaminating or hising the sample will be minimized.

Sare a portion of the sections used for cleanup as a blank. Taks 200 ml of this sections directly from the wash bottle being used and place it in a glass sample container labeled "actions 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 silicone gream, and cap the open outlet of the probe. Be

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

Condition No. I. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweeters and or clean disposable surgical sloves 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 restriction particulate matter and/or filter filter which adner to the filter holder rasket, by using a dry nylon brist brush and or a sharp-edged blade. Seal the container.

Course No. E. Taking care to see that duri on the outside of the probe or other curriors surfaced does not set into the sample, quantitatively recover particulate matter of the condensate from the probe mazie, probe

RULES AND REGULATIONS

fitting, probe liner, and from half of the fitter bolder by washing fices components with acctons and placing the wash in a glass concurrer. Distilled water may be used notes of sections when approved by the Administrator; and stail be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator.

and shall be used when specified by the Administrator; in these cases, ave a water biant and follow the Administrator; directions on acalysm. Perform the acason mass as follows:

Carfully remove the probe notice and clean the inside refore by making with sevione from a wash bottle and brushing with a nyloo brasis brush. Brush until the armone rises shows no table particles, atter which and rouse a final rings of the issue sources with accrone. Brush and rings the inside particles, atter which items as final rings of the issue sources with accrone. Brush and rings the inside sources by diffing and fitting with accrone in a similar way until no visible particles remain.

Prime the prime have with accrone by diffing and routing the probe while sourcing accrone into its upper and so that all inside surfaces will be wested with account of the inside surfaces will be wested with account a follow the actions runs with a probe brush. Hold the probe in an inclined position, squar account into the account runs with a probe brush. Hold the probe in an inclined position, squar account into the probe and as the probe brush is being pushed with a swissing action shrough the probe, and cutten any account and particulate matter which as brushed from the probe. Run the original pushed with a swissing action and particulate matter which as brushed from the probe lines and probes, and through in the above prescribed mainer at least six times since metal probes have small crevious in which particulate manner can be entrapped. Pines the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at the brush through in the above prescribed mainer at least six times since metal probes have small crevioes in which particulate mainer can be en

mm. Keep brushes clean and protected from contamination.

After snouring that all joints have been wiped clean
of sincone grease, clean the inside of the front half of the
sliter holder by rubbing the sinusces with a nivino britile
brish and rinsing with accume. 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 crycione, also (if applicable).
After all accisone washings and particulate matter have
been collected in the sample container. Tighten the lid
on the sample container so that accisone 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
get to determine if it has been competely spent and make
a notation of its condition. Transfer the stilica get from
the fourth impinger to its original container and seal.
A funnel may make it camer to pour the silica get without
spilling. A rubber politerinan may be used as an aid in
removing the silica get from the impinger. It is no
measure yto remove the small animing of dust particles
that may address to the impineer 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
fliquids to transfer the silica get. If is banned is available
in the field, follow the prox-dure for container No. 3
in Section 4.3.

Improve Halm. 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 there impingers to within

Improver Haler. Treat the impingers as follows: Make anotation of any color or film in the liquid extch. Measure the liquid which is in the first three impingers to within all mile by using a graduated cylinder or by weighing it is 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 efficient gas.

Discard the liquid siter measuring and recording the volume or weight, unless analysis of the impinger catch are other less Note, Section 2.1.7.

If a different type of condense is used, measure the amount of moisture condensed either volumetrically or gray meetically.

It a different type of countries in uses, measure amount of moisture condensed aither volumetrically or gravinetrically.

Whenever possible, containers should be shipped in such a way that 'ney remain upright at all times.

43. Analysis: Record the data required on a sheet such as the one shown in Figure 5-3. Randly each sample container as follows:

Container No. 1. Leave the contents in the shipping on the near or transfer the fitter and any loose particulate from the sample container to a tarved class weighing dish. Deviceate for 24 hours in a descention 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 toward weight less tark wright, whichever is greater, between two consecutive weightings, 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, mi	·
Acetone blank concentration, mg/mg (equation 5-4)	
Acetone wash blank, mg (equation 5-5)	
er e	

CONTAINER	WEIGHT OF PARTICULATE COLLECTED, mg								
NUMBER	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN						
1			٠.						
2									
TOTAL		÷							

		OF LIQUID OLLECTED
	IMPINGER VOLUME, ml.	SILICA GEL WEIGHT, 9
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* mi

^{*} Convert weight of water to volume by dividing total weight INCREASE BY DENSITY OF WATER (1g/ml):

INCREASE, g = VOLUME WATER, mi

Figure 5-3. Analytical data.

Alternatively, the sample may be oven dried at 105° C (200° F) for 2 to 3 hours, cooled in the desiceator, 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 (200° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight. Container No. 3. Note the level of liquid in the container

the sumps, and use this weight as a mai weight. Container No. 3. 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 sampae or use methods, subject to the approval of the Administrator, to currect the final results. Measure the liquid in this container either volumentically to ±1 mi or gravimetrically to ±0.5 g. Transfer the contents to a tared 250-mi beaker and evaporate to dryness at ambient temperature and pressure. Desiceste for 24 bours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Cantainer No. 3. Weigh the spent sillen gel for sillen gel plus impliner) to the nearest 0.5 g using a belance. This step may be conducted in the field.

"Action Elank" Container. Measure acctone in this container either volumerically or gravimetrically. Transfer the soctone to a tared 2.0-mi beaker and evaporate to dryness at ambient temperature and pressure.

Transfer the scetons to a tared 2.2-ml beaker and evaporate to dryness at ambient temperature and pressure Desiccate for 24 hours and weight to a contest 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 acctone blank container may be exported 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 swirted occasionally to maintain an event temperature. Use extreme care, as acctone is highly faminable and has a low dash point. fammable and has a low flash point.

S. Calibratio

Maintain a hiporatory log of all calibrations.
5.1 Probe Nozzie. Probe nozzies shall be calibrated before their Initial use in the field. Using a micrometer, measure the initial diameter of the nozzie to the nearest

0.025 mm (0.001 in.). Make three separate measuraments using different diameters each time, and obtain the average of the measuraments. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.), when notice become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each notice shall be permanently and uniquely identified.

use. Each nozze area to prove the first tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

Before its initial use in the field,

Section 4 of Method 2.

5.3 Metering System. Before its initial use in the field, the metering system stall be calibrated according to the procedure outlined in APTD-6578. Instead of physically adjusting the dry gas meter dish readings to correspond to the wet test meter readings, calibration factors may occured to mash annaturally correct the gas meter dish readings, to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted, for metering systems having disportage pumps, the normal lank-check procedure will not detect leakages within the pump. For these cases the foldowing leak-check procedure is suggested; make a 10-minute calibration run at 0.00057 m 1/min (0.02 cm); at the end of the run, take the difference of the measured was test meter run, take the difference of the measured wet test meter and dry gas meter rolumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00037 m #min (0.02 cm).

After each field use, the calibration of the metaring system shall be checked by performing three calibration runs at a single, intermediate ornice sering (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 west less mater 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, recambrate the meter over the full range of orifice settings, as outlined in APTD-0578.

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 confident values obtained before and after a test series differ by more than a percent the test series shall be performed using whichever meter coefficient value (i.a., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe-beating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0574. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0678 are used.

are used.

5.5 Temperature Gaures. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dust thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

scalinst mercury-in-class thermomenters.

5.5 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the ordice meter should be leak checked prior to initial use and siter each shipment. Leakage after the pump will result in less rolume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main raise on the present confinent a one-hole number stopper with number tubus, attached into the ordice exhaust pips. Disconnect and vent the low side of the ordice management. Close off the low side of ordice the presentate the system to 13 to 15 om (5 to 7 in.) water column by blowing into the rubber tubung. Punch of the tubong and observe the management for one minute. A loss of pressure on the management indicates a leak in the meter box; leaks, if present, must be corrected. be converted

5.7 Barometer, Calibrate aminat a mercury berometer.

Carry our raintalations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equiptions may be used as long as they give equivalent

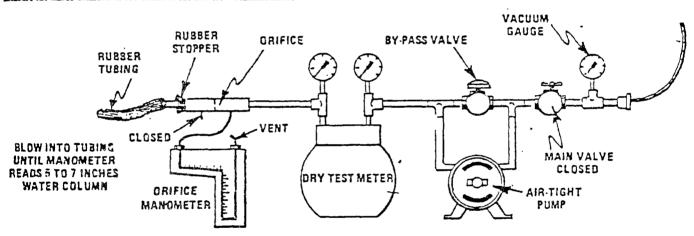


Figure 5-4. Leak check of meter box.

&1 Nomenciature

omenciature

—Cross-ectionsi area of nozzla, m³ (ft*).

—Water vapor in the gas stream, proportion
by volume.

—Acetose blank residue concentrations, mg/g.

= Concentration of particulate matter in stack gas, dry basis, corrected to standard condi-tions, g/dsom (g/dscf). = Percent of rockinetic sampling.

Percent of twinetic sampling.
 Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057
 ming in (0.02 cm) or 4 percent of the average sampling rate, whicherer is less.
 Individual leakage rate observed during the leak check conducted prior to the "ita" component change (i=1, 2, 3 »), mymin (cfm).

L m³/min (c/m).

mymin (cim).

Leakage rate observed during the post-test leak check, mi/min (cim).

Total amount of particulate maiter collected, L,

-Molecular weight of Water, 18.0 g/g-mole M.

(18.0 lb/lb-mole).

=Mass of residue of scenne after evaporation,

¿'ba

mg.

Burometric pressure at the sampling site, mm Hg (in. Hg).

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

Starth-d absolute pressure, 760 mm Hg (iv.92 in. Hg).

=Ideel gas constant, 0.06226 mm Hg-m^{1/2} K-g-mole (21.35 in. Hg-(1.4" R-lb-mole). =Absolute average dry gas meter temperature (see Figure 5-2), "K ("R).

R

(see Figure 5-2), K (*R).

T. Absolute a verse; stack gas temperature (see Figure 5-2), K (*R).

Test

Standard absolute temperature, 202* K (525* R).

Volume of acetone blank, ml.

Vi. Volume of acetone used in wash, ml.

Vi. Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

V = Volume of gas sample as measured by dry gas meter, dom (dcl).

V = (sid) = Volume of gas sample measured by the dry gas meter, corrected to standard conditions,

V=(sid) = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).
 V=(sid) = Volume of water vapor in the gas sample, corrected to standard conditions, sem (scf).
 V=Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (Usec).
 W= Weight of residue in acctone wash, mg.
 Y=Dry mas meter calibration factor.
 Af = Average pressure differential across the orfice meter (see Figure 5-2), mm H₂O (in. H₂O).
 p= Deussty of acctone, mg.ml (see label on bottle).

bottle). .-Density of water, 0.9982 g/ml (0.002201

#= Total sampling time, min.

*8:-Sampling time interval, from the beginning of a run until the first component change, min.

9. Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, mun.

changes, min.

#,=Sampling time interval, from the final (nth)
component change until the end of the
sampling run, min.

13.5=Specific gravity of mercury.

60=Sec/min.

100=Conversion to percent.

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

6.1 Dry Gas Volume. Correct the sample volume
measured by the dry gas meter to standard conditions
(20° C, 750 mm Hg or 63° F, 29.92 in. Hg) by using
Ennation 5-1.

$$\begin{aligned} V_{m,(e\times d)} &= V_m Y \left(\frac{T_{etd}}{T_m} \right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{end}} \right] \\ &= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_-} \end{aligned}$$

Econtion 5-1

where: mi=0.3648 "K/mm Hg for metric units =17.64 "R/m. Hg for English units

Norm.—Equation 5-1 can be used as written unless the (askare rate observed during any of the mandatory leak theoric (i.e., the post-test leak check or leak checks conducted prior to component changes) stresds L_w If L_w or L_w ascessis L_w. Equation 5-1 must be modified as follows:

(a) Case L No component changes made during sampling run. In this case, replace Va in Equation 5-1 with the expression;

$$V_{\bullet} - (L_{\bullet} - L_{\bullet}) \delta$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_{α} in Equation 5-3 by the expression:

$$\begin{bmatrix} V_n - (L_1 - L_n)\theta_1 \\ -\sum_{i=2}^n (L_i - L_n)\theta_{i-1} (L_p - L_n)\theta_p \end{bmatrix}$$

and substitute only for those leakage rates (Li or $L_{\rm p}$) which exceed $L_{\rm m}$

6.4 Volume of water vapor.

Equation 5-2
$$V_{\text{w(and)}} = V_{1s} \left(\frac{\rho_{\text{w}}}{M_{\text{w}}} \right) \left(\frac{RT_{\text{and}}}{P_{\text{and}}} \right) = K_1 V_{1s}$$

where:

K:=0.001333 m²/ml for metric units

=0.04707 ft=ml for English units.

8.5 Moisture Content.

$$B_{\sigma\sigma} = \frac{V_{\sigma \text{ (ord)}}}{V_{\pi \text{ (ord)}} + V_{\sigma \text{ (ord)}}}$$

Nors.—In metasted or water dropiet-laden passivement, two calculations of the moisture content of the stack passive be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of ministed conductors. The lower of the two values of B.— shall be considered correct. The procedure for detaining the conduction of the conduction In the routine contact based upon assumption of saturated conditions is given in the Note of Section 1.2 of Niethod 4. For the purposes of this method, the average stack gas temperature from Figure 3-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor $u \pm 1^{\circ}$ C (u° F).

6.6 Acctone Blank Concentration.

$$C_{\circ} = \frac{m_{\circ}}{\Gamma_{\circ} a_{\circ}}$$

Enuation 5-4

Equation 5-4

6.7 Acetone Wish Blank.

$$W_{\bullet} = C_{\bullet} V_{\bullet \bullet} \rho_{\bullet}$$

6.3 Total Particulate Weight. Detarmine the total particulate calch from the sum of the weight obtained from containers I and 2 less the account blank uses Figure 5-3). Note.—Relar to Section 4.1.3 to asset in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_{*}=(0.001 \ g/mg) \ (m_{*}/V_{m(sed)})$$

6.10 Conversion Factors:

		·
From	To	Malaply by
sc!	m	0, 02832
ecf g;it ^a g/ft ^a g/ft ^a	gr/ft ^a	15. 43 2. 205 × 10 ⁻⁴
C/IL)	€/m³	37.31

Equation 5-3

6.11 Isolainetic Variation.
6.11.1 Calculation From Raw Data.

$$I = \frac{100 \ T_{\bullet}[K_{\bullet}V_{1\bullet} + (V_{\bullet}/T_{\bullet}) \ (P_{ber} + \Delta B/13.6)]}{60 \ \theta v_{\bullet} P_{\bullet} A_{\bullet}}$$

here: $H_1=0.001454$ mm $H_2=mVml-^*K$ for metric unita =0.007559 in. $H_3=(17m)-^*R$ for English unita. 6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_{\bullet}V_{\bullet}(\omega_0)P_{\bullet\omega}100}{T_{\bullet\omega}r_{\bullet}\theta A_{\bullet}P_{\bullet}60(1-B_{\bullet\sigma})}$$
$$= K_{\bullet}\frac{T_{\bullet}V_{\bullet}(\omega_0)}{P_{\bullet}V_{\bullet}A_{\bullet}\theta(1-B_{\bullet\sigma})}$$

There:

 $H_{i}=4.330$ for metric units =0.00450 for English units. 6.13 Acceptable Results. If 90 percent $\leq I \leq$ 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make judgments. Otherwise, reject the results and repeat the test.

7. Billingraphy

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D 6-DETERMINATION OF SULFUR I METROD & DIOXIDE

Equation 5-8 1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The sulfure acid must including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the baruum-thorin turation method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detertable limit of the method.

determination of sulfur diaride emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of \$00/m³ (2.12×10⁻⁴ 1b/ft 4). Although no upper limit has been established, tests have shown that concentrations as high as \$0,000 mg/m³ of \$00; can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 pm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about \$3,000 mg/m³.

concentration limit in a fibriter sample is should be, and my, my.

Possible interferents are free ammonia, water-soluble cations, and finorides. The cauons and finorides are removed by glass wool filters and an isopropasiol bubbler, and hence do not affect the BO, analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic turnes (such as in inlets to courted devices), a high-efficiency glass fiber filter must be used in piace-of the glass wool ping (i.e., the one in the probe) to remove the cation interferents.

Free ammonia interferes by reacting with SOs 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 nutting white particulate matter in the probe and isopropanol bubbler), siterostive methods, subject to the approval of the Administrator, U.B. Environmental Protection Agency, we required.

required.

2 Apparetus

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 <u>Sampling Train</u>. 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 \leq 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,

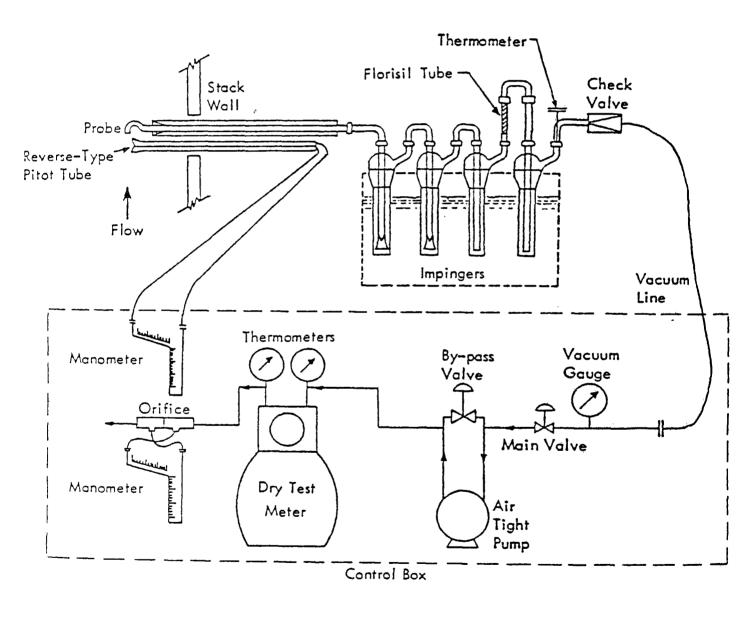


Figure A-1. PCB Sampling Train for Incinerators

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 (\sim 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^{\oplus} wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.
- 5.2.3 Sample storage containers--Glass bottles, I liter, with $\text{TFE}^{\scriptsize\textcircled{3}}\text{-lined}$ screw caps.
 - 5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.
 - 5.2.5 Aluminum foil--Heavy duty.

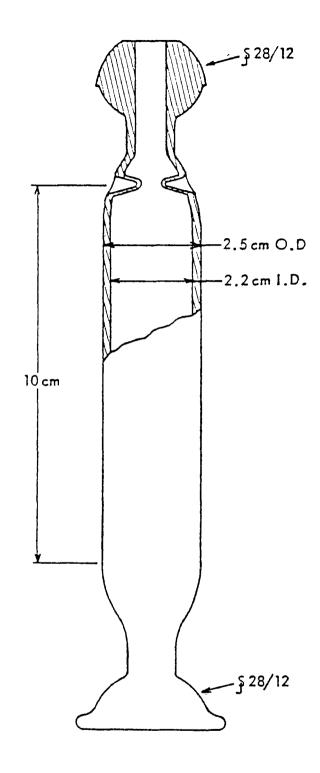


Figure A-2. Florisil Adsorbent Tube

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 g condenser, 24/40 g 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 $^{\odot}$).
 - 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 $^{\oplus}$ -lined screw cap.
- 6.1.3 Water--Deionized, then glass-distilled, and stored in hexanerinsed glass containers with $TFE^{\textcircled{\tiny 0}}$ -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 hexanerinsed glass containers with TFE®-lined screw caps.

- 6.3.4 Sodium sulfate (Na₂SO₄)--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 (SbCl₅)--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 save 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 the 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 m³/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 \pm 0.02 coefficients ($C_{\rm p}$), and when sampling in air or a stack gas with equivalent density (molecular weight, $\rm M_d$, equal to 29 \pm 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 $\rm C_{\rm p}$ and $\rm M_{\rm d}$ 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 I 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.

PLANT	
DATE	
SAMPLING LOCATION	
SAMPLE TYPE	
RUN NUMBER	
OPERATOR	
AMBIENT TEMPERATURE	
BAROMETRIC PRESSURE	
STATIC PRESSURE, (P ₃)	
FILTER NUMBER (s)	

PROBE LENGTH AND TYPE
NOZZLE I D
ASSUMED MOISTURE. *
SAMPLE BOX NUMBER
METER BOX NUMBER
METER AH
C FACTOR
PROBE HEATER SETTING
HEATER BOX SETTING
REFERENCE Ap

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY_____ MINUTES

TRAVERSE POINT NUMBER	CLOCK TIME (24 h) CLOCK)	GAS METER READING (V _m), II ³	VELOCITY HEAD (Δρ ₅), in, H ₂ O	DIFFER	PRESSURE ENTIAL n. 11 ₂ 0)	STACK TEMPERATURE (T _s),"F	TEMPE	S METER RATURE	PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE. °F	IMPINGER TEMPERATUS:
HORIDER	TIME, min		(Δρ ₅), iii. 11 ₂ 0	DESIRED	,	('s'. '	INLET (T _{m in}), °F	OUTLET (T _{m oul}).°F			
								-			
				<u> </u>	<u> </u>						
											•

COMMENTS

Figure A-3. Field Data Sheet

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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 <u>Sample recovery</u>. 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 $0.0057 \, \mathrm{m}^3/\mathrm{min}$ (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), pg.
- $G_s = Total$ weight of PCBs (as DCB) in sample, μg .
- C_s = Concentration of PCBs in stack gas, $\mu g/m^3$, 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 (ft²).
- 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 $Hg-m^3/^\circ K-g-mole$ (21.83 in. $Hg-ft^3/^\circ R-lb-mole$).
 - T_m = Absolute average dry gas meter temperature °K (°R).
 - T_c = 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 l 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. = Total volume of sample, ml.
 - V = 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).
 - $\rho_{\rm W}$ = 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 Drv gas volume. Correct the sample volume measured by the dry gas meter to standard conditions $[20^{\circ}\text{C}, 760 \text{ mm Hg} (68^{\circ}\text{F}, 29.92 \text{ in. Hg})]$ 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

$$V_{w(std)} = V_{lc} \frac{\rho_{w}}{M_{w}} \frac{RT_{std}}{P_{std}} = K V_{lc}$$
 Equation A-2

where $K = 0.00134 \text{ m}^3/\text{ml}$ for metric units = $0.0472 \text{ ft}^3/\text{ml}$ 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.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3}$$

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.

$$C_s = K \frac{G_s}{V_{m(std)}}$$

Equation A-5

where
$$K = 35.31 \text{ ft}^3/\text{m}^3$$

9.7 <u>Isokinetic variation</u>

9.7.1 Calculations from raw data.

$$I = \frac{100 \text{ T}_{s} [\text{K V}_{1c} + (\text{V}_{m}/\text{T}_{m}) (\text{P}_{bar}) + \Delta \text{H}/13.6)]}{60 \text{ 0 V}_{s} P_{s} A_{p}}$$

Equation A-6

where

$$K = 0.00346$$
 mm $Hg-m^3/ml-^{\circ}K$ for metric units
= 0.00267 in. $Hg-ft^3/ml-^{\circ}R$ for English units

9.7.2 Calculations from intermediate values.

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

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

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 <u>Sampling moisture saturated or supersaturated stack gases.</u> 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 <u>PCB verification</u>. 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

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Attachment F

Determination of Nitrogen Oxide Emissions from Stationary Sources

33.5 Sulfuric Acid Standard, 0.0100 N. Purchase or sandardise to \$0.0002 N arrainst 0.0100 N Na0 A which he previously been standardized assures potactium gid pitchalate (primary standard grade).

i Procedure

4.1 Sampling.
4.1.1 Preparation of collection train. Measure 15 ml of appearst isopropanol into the midgat bubbles and 15 ml of 3 percent hydrogen peroxide into each of the first pre-midget impringer for Assemble the train as abown in Figure 6.1. Adjust probe caster to a temperature sufficient to prevent water ameliesation. Place crushed ice and water around the Propriete ...

Leak-check procedure. A leak check prior to the is opconal; how ampling run is optional; however, a lenk check after the ampling run is mandatory. The leak-check procedure is

schlows:

What he probe disconnected, place a vacuum sauge at the high to the bubbler and buil a vacuum of 250 mm 00lm.) Hg; ping or plach of the outlet of the flow meter, and then turn off the pump. The vacuum shall remain table for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter and to prefet back flow of the implicate fluid.

recum gains before releasing the flow meter end to present back flow of the implicate fluid.

Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental frotection Agency. The procedure used in Method 5 is not untable for displication. Excord the Initial dry ras meter reading and he omegate pressure. To begin sampling, position the flood the probe at the sampling point, connect the prope to the bubbler, and start the primp. Admit the sampling flow to a constant rate of approximately 1.0 Upstimin as indicated by the rotameter. Haintain this constant rate of earlier sampling roun. This readings (dry gas meter, temperatures at dry growness and at impinger outlet and rate meter) at earlier every 5 minutes. Add more see learning the last impirizer at 20°C (65°F) or less. At the conclusion of each run, turn of the primp, remove probe from the stack, and record the final readings. Conduct a last check as in Section 4.1.2. (This leak check is mandatory) If a tesk is found, void the test run. Drain the ice last, and purse the remaining part of the train by drawing class ambient air through the system for 15 minutes at the sampling rate.

is crean information through the system in a limit of the state of the sampling rate.

Clean ambient sir can be provided by passing air through a charcosi filter or through an extra midget impinger with 15 ml of 3 percent E/O₂. The tester may out to simply use ambient air, without purification.

4.2 Sample Recovery, Discorribet the impurgers after purping. Discord the contants of the midget bubbler. Pour the contants of the midget subbler. Pour

puring. Discard the contents of the midget Subbier. Four the contents of the midget implurers into a leak-dree polyethylene bottle for shipmant. Binse the three midget impingers and the connecting tubes with deionized, distilled water, and add the washings to the same storage outsiner. Mark the fluid level, Seel and identify the sample container.

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

Translet the contents of the storage container to a

trator, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask and directs to exactly 100 ml with defonized, distilled water. Pipette a 20-ml aliquot of this soliton into a 250-ml Edenmeyer flask, add 80 ml of 100 percent isopropenol and two to four drops of thorin indicator, and tirate to a pink andpoint using 0.0100 N brium perchlorate. Repeat and average the tirration volumes. Run a blank with each series of samples. Reptical tire those more a research of 2 ml. cate directions must agree within 1 percent or 0.2 mi, whichever is larger.

(Norg.--Protect the 0.0100 N barium perchlorate solution from eraporation at all times.)

6. Calibration

3.1 Metering System.
3.1.1 Initial Calibration. Before its initial use in the field first leak check the metering system (drying tube, people valve, pump, rotameter, and dry gas meter) as

follows: place a vacuum gauge at the inlet to the drying rube and pull a vacuum of 250 mm (10 in.) Hg; plug or rube and pull a vacuum of 250 mm (10 in.) Hg; plug or rube and pull a vacuum of 250 mm (10 in.) Hg; plug or ripinch off the outlet or the flow meter, and then turn of the pump. The vacuum shall remain wable 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 flow the drying tube. Make three independant calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (west test meter calibration volumes dyinded by the dry gas meter volume, both volumes adjusted to the same reference tamperature and tressure), for each run, and average the results. If any Y value deviates by more than 2 persons from the average, the metaning system is unacceptable for use. Otherwise, use the average at the calibration factor for subsequent taxt runs.

5.1.2 Post-Test Calibration Cheez, Allier each field test series, conduct a calibration cheex 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 mater 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 Gry gas metable. If the calibration factor deviates by more strain of severe severe.

day gas metar volumes obtained during the test sense are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 3.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas religious for such feet min.

factor (initial or recairement)
rolume for each test run.
Thermometers. Calibrate against marcury 5.2 Thermometers. Calibrate against marcury-to-glass thermometers.
5.3 Rotsmeter. 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 barom-

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

6. Calculations

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

Nomenciature.

Cas = Concentration of sulfur dioxide, dry besis corrected to standard conditions, mg/dxm (lb/dscn).

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

P. Barometre pressure at the crit ordice of the dry gas mater, mm Hz (in Hz).

Pressured absolute pressure, 760 mm Hz
(29.2 in Hz).

T.= Average dry gas meter absolute temperature, "K ('R).
Taum Standard absolute temperature, "M" K (128° B).

(\$135" B).

V.=Volume of sample allquot titrated, ml.

V.=Dry gas volume as measured by the dry gas meter, dem (def).

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

cscm (dsci).

Visite = Treat volume of solution in which the sulfar dioxide sample is contained, 100 mi.

Vi=Volume of barium perchlorate titrant csed for the sample, mi (average of replicate titrant).

for the sample, mi (average of replicate titrations).

Vise Volume of barium perchlorate titrant used for the biank, mi.

Y=Dry gas meter-calibration factor.

22.C3 = Equivalent weight of sulfur dioxide.

6.2 Dry sample gas volume, corrected to standard conditions.

 $V_{\text{m (aid)}} = V_{\text{m}} Y \left(\frac{T_{\text{old}}}{T_{\text{m}}} \right) \left(\frac{P_{\text{bar}}}{P_{\text{aid}}} \right) = K_{1} Y \frac{V_{\text{m}} P_{\text{bar}}}{T_{\text{m}}}$

Equation 6-1

K₁=0.338 ° E/mm Hg for metric units, =17.64 ° R/m. Hg for English units, 6.3 Sulfur dioxide expoentration.

$$C_{6O_2} = K_2 \frac{(V_i - V_{ib}) N\left(\frac{V_{solu}}{V_o}\right)}{V_{m(scol)}}$$

Econtina 6-2

K=22.03 ms/meq. for metric units. =7.051×10⁻¹ lb/meq. for English units.

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METHOD 7-DETERMINATION OF NITSOURN ORDER-EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A grab sample is collected in an example of fask containing a dilute suifune acid-bydrogen peroxide absorbing solution, and the nitrigen modes, except nitrous oxide, are measured colorimetrically using the phenoidisuitonio acid (PD3) procedure.

1.2 Applicability. This method is applicable to the measurement of nigrores oxides emitted from stationary sources. The range of the method has been determine to be 2 to 400 milligrams NO₂ (as NO₂) per dry standar cubic meter, without having to dilute the sample.

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring ample volume to within ±20 percent and collecting a sample volume to allow analytical reproducibility to within ±5 percent, will be considered acceptable afternatives, subject to approval of the Administrator, U.S. Environmental Protection Agency. The following explanation and approval to making the protection of the production of the production of the protection of the production of equipment is used in sampling:

equipment is used in sampling:

2.1.1 Probe. Borodilisate glass tribing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a ping of glass wool is satisfactory for this purpose). Stainless stool or Tefon a 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 Pretection Agency.

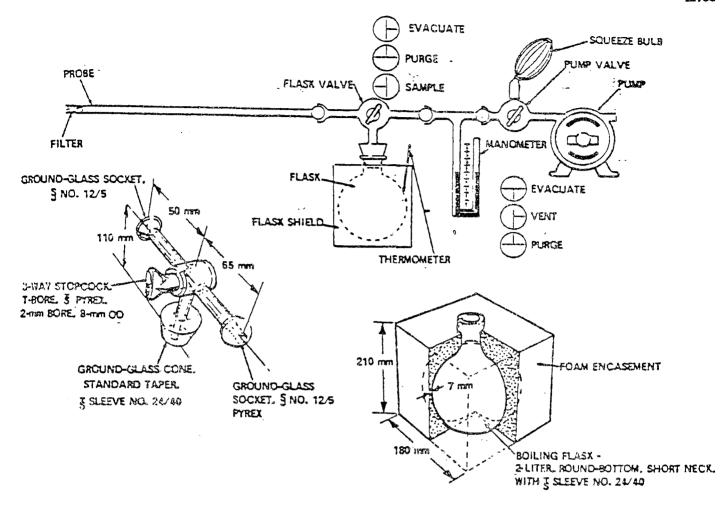


Figure 7-1. Samoling train, flask valve, and flask.

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

- 24.40 standard taper joint.

 2.1.4 Temperature Gauga, Dial-type thermometer, or other temperature gauga, capabla 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 stoppeck.

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

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

 21.8 Squeete Bulb. One-way.

 21.9 Volumettic Pipette. 25 ml.

 21.10 Estoprock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-35 has been found to be effective.

 21.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmosphene pressure to within 25 mm Hg (0.1 in. Hg). In many cases, the barometric resulting may be obtuined from a nearby national weather resulting may be obtuined from a nearby national weather resulting that the shoolute 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 2.3 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase, or vice versa for elevation decrease.

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

 23.1 Graduated Cyllinder. So mi with 1-mi divisions.

 22.2 Storage Containers. Leak free polyethylene bottles.

- 2.2.3 Wash Bottle. Polysthylens of similar 2.2.4 Glass Stirring Rod.
 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:

 Notemetric Pipettes. Two 1 ml, two 2 ml, one 2 ml of each sample
- 2.3.1 Volumetric Pipettes. Two 1 ml, two 2 ml, one 1 ml, one 4 ml, two 10 ml, and one 25 ml for each sample

- Porcelain Bysporating Dishes, 175- to 250-mi 2.1.2 Porosiain Byaporating Dishes, 173- to 250-mi capacity with lip for pouring, one for each mample and each standard. The Coors No. 45006 (shallow-form, 193 mi) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Naige No. 1203, 150 mi), 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 stor, the solids should be removed by filtration (see Section 4.3).

 2.1.3 Steam Bath. Low-temperature overs or thermostatically controlled hot plates kept below 70° C (160° P) are acceptable alternatives.

 2.1.4 Dropoung Pipette or Dropper, Three required.

- are acceptable atternatives.

 2.3.4 Dropping Pipette or Dropper. Three required.

 2.2.5 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 ENO; solution), and 1000 ml (one).
- 3.8 Spectrophotometer. To measure absorbance at 410 nm.
- 2.3.9 Oradinated 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

3. Persoents

- 3. Respenis

 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 svailable grade.

 3.1 Sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated HisO1 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 surlight.

 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 liser.
- in deionized, distilled water and dilute to 1 liter.

 3.2.2 Water. Descrized, distilled to conform to ASTM specification Di193-74, Type 1. At the option of the

- analyst, the KMNO, test for outlisable occasio matter may be united when high concentrations of organic matter are not orported to be present.

 3.1 Analysis For the abelysis, the following reagents

- 2.3. Analysis. For the analysis, the following reagents are required:
 3.3.1 Firming Sulturic Acid. 15 to 13 percent by weight free sailur trioxide. HANDLE WITH CAUTION.
 3.3.2 Febroi. White solid.
 3.3.3 Sulfure Acid. Concentrated, 95 percent minimum assey. HANDLE WITH CAUTION.
 3.3.4 Potassium Nitrate. Dried at 105 to 110° C (220 to 220° F) for a minimum of 2 hours just prior to preparation of standard solution.
 3.1.5 Standard KNO; Solution. Dissolve exactly 2198 go dired potassium nitrate (ENO;) in deionized, distilled water and dilute to 1 licar with delonized, distilled water and tilute to 10 licar with delonized, distilled water and solution to 100 ml with denonized distilled water in a 1,000-ml volumetric dast.
 3.1.6 Working Standard KNO; Solution. Dilute 10 ml of the standard Solution to 100 ml with denonized distilled water. One milliliter of the working standard solution is equivalent to 100 ml altrogen dioxide (NO;).
 3.3.7 Water. Denonized, distilled as in Section 1.2.2.
 3.3.3 Phenoidisulloue Acid Solution. Dissolve 25 go pure white phecol in 150 ml concentrated silfuric acid on a steam bath. Cool, add 73 ml furning sulfuric acid, and best at 100° C (212° F) for 2 hours. Store in 2 dark stoppered bottle.

4. Procedures

4.1 Sampling.

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 view supper 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 greated with a high-vacuum, high-temperature chloredulorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuation the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the valour pressure of waters at the ensurar temperature is desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manageter for any pressure fluctuation. (Any variation

greater than 10 mm. Hg (0.4 in. Hg) ever a period of 1 minute is not acceptable, and the flak's is not to be used until the leakage problem is corrected. Fressure in the flak's is not to encoed 75 mm Hg (10 in. Hg) absolute at the time sampling a commenced.) Record the volume at the time sampling a commenced.) Record the volume at the time sampling a commenced.) Record the volume of the flak's and valve (1/1), the flak's temperature (T.), and the barymotric pressure. Turn the flak's valve counterclockwas to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum mice dange the squases built. If condansation cours in the probe and the visit valve area, heat the probe and purse until the condansation disappears. Not, turn the pump valve to its "vent" position. Turn the flak's valve clockwase to its "worker" position. Turn the flak's valve clockwase to its "worker" position. Turn the flak's valve clockwase in the flak's valve to the manouncier. The absolute internal pressure less the manouncier. The absolute internal pressure is the flak's until pressure in the flak's until pressure in the flak's and rample into (i.e., duce, stack) are equal. This will untilly require about 15 seconds, a longer pariod indicates a "plur" in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the probe, which must be corrected before samples (in the flak's valve to its "purge" position and disconnect the flake valve to its "purge" position and disconnect the flake valve to its "purge" to the samples must be limediumed in the flake in the flake to the samples of a calibration gas minuture of NO in Ni), then errectually for the conversion of NO to NO, (e.g., an applicable subpart of the standard may require taking a sample of a calibra

acmospheric pressure.

atmospheric pressure.

4.2 Sample Recovery Lot the final set for a minimum of 16 hours and than shake the contents for 2 minimum. One the final to a marriary filled U-tube manometer. Open the valve from the finals to the manometer and record the finals temperature (T/), the barometric pressure, and the difference between the marriary levels to the manometer. The absolute internal pressure in the manometer The strength of the finals to be leaffered polyectyleme bottle. Since the finals to be leaffere polyectyleme bottle. Since the first value and the manometer results to the finals to be leaffere polyectyleme bottle. Since the first value and the manometer and the first to be leaffered when the polyectyleme bottle. Attributed values and edited for the water to the bottle. Adjust the pill to between 9 and 12 by adding socium hydrouded (IN), dropvetse (About 23 to 83 drops). Check the pill by dippular a chount of the first the pill by dippular a (about 2) to 83 drops). Check the pE by dipping a suring red into the column and then touching the red to the pE test paper. Remove as little materials as possible during this step. Mark the begins of the liquid level so that the container can be concerned for leakings after transport. Label the container to clearly identify its container. Send the container for shipping.

content. Sent the extrainer or supporty.

4.3 Analysis. Note the level of the liquid in container and condition whether at not only completives lost during shipment; note this on the analysical data sheet. If a notified amount of leakage has contried, either via the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediate the state of the sample of the s noticeable amount of leakage has caustred, either void the authoritor to active a party of the approval of the Administrator, to convert the hinsi results. Immediately prior to analysis, transfer the contents of the hipping contenier to a 50-ml volument flask, and mass the container to be of the flask, and mass the container to be of the flask, and difficulted water. Add the rine water to the flask and difficulted water, with deloniesd, distilled water, mix incorogish? Piperte a 25-ml aliquoe into the processin evaporation dain. Nexura any timesed portion of the sample to the polyethylane starage bottle. Evaporation 25-ml aniquot to dryness on a steam both and show to cool. Add 2 ml. obscioldistrationle and solution to the dried residues and timese theroughly with a poylethylene policeman. Make sure the solution contacts all the reades. Add 1 ml decontact, distilled water and four drops of concentrated sulfume add. Hent the solution on a steam bath for 3 minutes with occasional surring. Abov the colution to cool, add 20 ml defouted, distilled water, mix wall by stirring, and add concentrated ammonium hydrousde, dropwiss, with constant stirring, until the pE is 10 (as determined by pH poper). If the sample contains solids, these must be removed by filtration (centralization is an acceptable alternative, subject to the soproval of the Administrator), as follows: filter through Hastman No. 41 filter paper into a 100-ml volument flask; thus the evaporating dish with three firms contains of deconited, distilled water, filter these three firms. Wash the niter with at least three 15-ml portions of deconited, distilled water, filter these three firms. Wash the niter with at least three 15-ml portions of deconited, distilled water; filter these three firms as weath the solution can be transferred directly or the 100-ml volumenter flask and dilute to the mark with delonized, distilled water; filter these three firms of the other with delonized distilled water. If solids are about the observe the absorbance at the fortuna

31 Flick Volume The volume of the collection flash-from rains combination must be known prior to sam-pher. Assemble the flesh and flash value and fill with

water, to the stoppock. Measure the volume of water to ±10 ml. Record this volume on the flask.

water, to the stopeock. Making the volume of water \$2.10 ml. Record this volume on the flask.

\$2.2 Spectrophotomoler Calibration

\$5.2.1 Optimum Vis velenth Determination. For both fired and variable wavelength spectrophotometers, scalibrate scaling standard certified vavelength of 410 mm, every 6 months. Alternatively, for variable wavelength spectrophotomolers, scan the spectrum between 400 and 415 mm using a 200 at NO 1 standard solution (see Section 6.2.2). If a peak does not occur, the spectrophotometer is probably matrunctioning, and should be repaired. When a peak is obtained within the 400 to 415 mm range, the wavelength at which this peak occurs shall be repaired. When a peak is obtained within the 400 to 415 mm range, the wavelength at which this peak occurs shall be solvened for both the standards and samples.

\$2.2 Determination of Spectrophotometer Calibration Factor & Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of the ENO; working standard solution (1 ml = 100 at NO) to a series of five porceisur evaporating dishes. To each, add 23 ml of absorbing solution, 10 ml detonized, distilled water, and codium hydroxido (1N), dropwise, until the pH is between 9 and 12 (about 25 to 35 drops each).

water, and codium hydroxido (1N), dropwiss, that the pH is between 9 and 12 (about 23 to 33 drops each). Bedinning with the evaporation step, follow the analysis procedure of Section 4.2, until the solution has been transferred to the 100 ml volume tric flask and diluted to the mark. Measure the absorbance of each solution, at the obtunum wavelength, as determined in Section 5.21. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer cambration factor as follows:

$$K_{e} = 100 \frac{A_{1} + 2A_{2} + 3A_{6} + 4A_{4}}{A_{1}^{2} + A_{5}^{2} + A_{5}^{3} + A_{6}^{3}}$$

Equation 7-1

where:

K.= Calibration factor

A.= Absorbance of the 100-sg NO; standard

A.= Absorbance of the 220-sg NO; standard

A.= Absorbance of the 300-sg NO; standard

A.= Absorbance of the 400-sg NO; standard

5.3 Barometer. Calibrate egainst a mercury barom-

six.
5.4 Temperature Osuge, Calibrate dial thermometers against mercury-to-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

A. Oslowlations

Carry out the calculations, retaining at least one error decumal figure beyond that of the acquired data. Round off figures after firml calculations.
One content of the acquired data. Round off figures after firml calculations.
Nomenclature.
A = Absorbance of sample.
C = Concentration of NO. as NO. dry basis, corrected to standard conditions, mg.dxcm (lbidxcf).
F = Dinton factor (i.e., 28/8, 28/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).
K. = Spectrophotometer calibration factor.
E = Hass of NO. as NO. in gas sample, pf.
Pr. = Final absolute pressure of flask, mm Hg (in. Hg).
Pr. = Standard absolute pressure, 750 mm Hg (29.92 in. Hg).
T = Final absolute temperature of flask, "K (*R).

Hg).

The Final absolute temperature of flask, *K (*R).

The Final absolute temperature of flask, *K (*R).

The Standard absolute temperature, 257 % (528 R).

The Standard absolute temperature, 257 % (528 R).

The Standard absolute temperature, 257 % (528 R).

Description of flask and valve, mi.

V = Volume of flask and valve, mi.

V = Volume of flask and valve, mi.

2 = 56723, the almost factor. (If other than a 25-ml almost was used for analysis, the corresponding factor must be substituted).

8.2 Eample volume, dry basis, corrected to standard conditions.

$$\begin{split} V_{ss} &= \frac{T_{std}}{P_{std}} \; (V_f - V_s) \; \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \\ &= K_i (V_f - 25 \; \text{ml}) \; \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \end{split}$$

Equation 7-2

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

= 17.64 $\frac{^{\circ}R}{\text{in. Hg}}$ for Euglish units

6.3 Total my NO: per sample.

$$m=2K_{\star}AF$$

Equation 7-3

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

5.4 Sample concentration, dry basis, corrected to standard conditions

$$C=K_1$$
 $\frac{m}{V_{ac}}$

Equation 7-4

where:

$$K_1 = 10^3 \frac{\text{mg/m}^3}{\mu \text{g/ml}}$$
 for metric units

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

METHOD 3-DETERMINATION OF SULFULIC ACTO MISS AND SULFUE DIOXIDE EXCESSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted isoldnotically from the stack. The sulfune and mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barron-thorin uration method.

1.2 Applicability. This method is applicable for the determination of sulfure acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from successful successful control of the successful success Collaborative term have shown that the minimum detectable limits of the method are 0.05 milligrams/cubbe meter (0.03):10⁻¹ pounds/cuble foot) for sulfur morids and 1.2 mg/m³ (0.74 - 10⁻¹ lb/ft*) for sulfur dioxida. No upper limits have been established. Besed on theoretical calculations for 200 millilitars of 3 persons bydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (3.5 ft²) gas sample is about 12.500 mg/m³ (7.7×10⁻¹ lb/ft²). The upper limit can be attended by increasing the graphity of recording similar. extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are finorides, free ammonia, and dimethyl anilina. 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.

Fiterable particulate matter may be determined along with 80; and 80; (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.

2.1 Sampling. A schematic of the campling 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 needed. Commercial models of this train are available. For those who desire to build their own, however, complete one-struction details are described in APTD-0681. Changes from the APTD-0681 document and allowable modifications to Figure 8-1 are discussed in the following subsections. subsections.

subsections.

The operating and maintenance procedures for the sampling train are described in APTD-576. Since correct usage is important in obtaining valid results, all users should read the APTD-576 document and adopt the operating and maintenance procedures outlined to 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 Notale, Same as Method 5, Section 2.1.1.
2.1.2 Probe Liner, Beroslicate or quarts gizes, with 6 heading system to greens wishle conductation during

besting system to prevent visible condensation during sampling. Do not use metal probe liners.

21.3 Pitot Tube. Same as Method 5, Section 21.3.

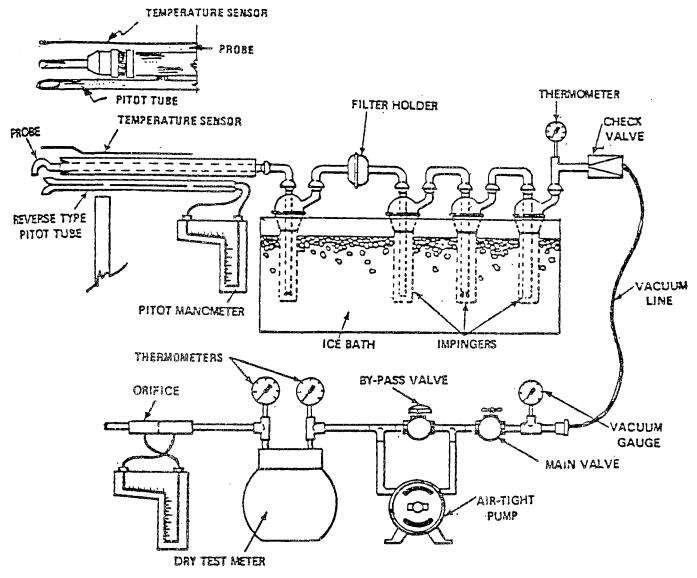


Figure 8-1: Sulfuric acid mist sampling train.

21.4 Differential Pressure Gauge, Same as Method 5,

21.4 Differential Pressure Gauge. Same as Method 5, Section 2.1.4.
21.3 Filter Holder. Borodilicato glass, with a glass lift filter support and a silicone rubber gasket. Other gasket materials, e.g., Tesion or Viton, may be used subset to the approval of the Administrator. The holder darm 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.
21.6 Impingent—Four, as shown in Figure 8-1. The first and third simil be of the Greenburg-Smith design with standard tips. The second and fourth 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 (25 in.) from the bottom of the fask. Smills collection systems, which have been approved by the Administrator, may be used. trator, may be used.
21.7 Metering System. Same as Method 3, Section

2.1.3 Barometer, Same as Method 3, Section 2.1.9.
2.1.9 Gas Density Determination Education. Section 2.1.9. 2.19 Gas Density Determination Equipment, Same as Methol 5, Section 2.1.10. Temperature Gauge. Thermometer, or equiva-

14.10 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, 510 ml. (two).

(two).

2.7.2 Oraduated Cylinders, 250 ml, 1 liter. (Volumetric flacks tray also be used.)

223 Storage Bottles, Leak-free polyethylens 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 Eurrette. 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.

±0.5 g.
2.3.6 Dropping Bottle. To add indicator solution, 125-ml siza.

3. Reasents

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

the best available grade.

3.1 Sampling.

3.1.1 Filters, Same as Method 5, Section 3.1.1.

3.1.2 Filters, Same as Method 5, Section 3.1.2.

3.1.3 Water, Delonized, distribed to conform to ASTM specification Dil93-74, Type 1. At the option of the analyst, the XMnO, 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 delonized, 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 impunities that will cause er-

roneomiy high sulfuric soid mist measurement. Use the following tast for detecting peroxides in each lot of isopropanol: Shake 10 mi of the isopropanol with 10 mi of freship prepared 10 percent potassium lodide solution. Prepare a black by similarly treating 10 mi of distilled water. After i minute, read the absorbance on a spectrophotometer at 352 nanometers. If the absorbance encoeds 0.1, the isopropanol shall not be used. Peroxides may be removed from isopropanol by redistilling, or by passage through a column of activated shamina. However, reagent-grad-isopropanol with suitably low peroxide levels is madily available from commercial sources; therefore, relection of contaminated loss may be more efficient than following the peroxide, 3 Percent. Dilute 100 mi of 30 percent hydrogen peroxide, 3 Percent. Dilute 100 mi of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water. Prepare fresh daily.

3.1.6 Crushed Ica.

3.2 Eample Recovery.

3.2.1 Water. Same as 3.1.2

3.2.2 Isopropanol, 100 Percent.

3.3.3 Thorn Indicator. 1-(o-arsonophenylaso)-2-asphthol-3, 6-distillonic soid, disodium sait, or equivalent. Dissoive 0.20 g in 100 mi of deionized, distilled water.

3.3.4 Barium Perchiorate (0.0100 Normal), Dissoive 1.55 g of barium perchiorate (0.0100 Normal). Dissoive (18aCl-2H-2) may be used instead of the barium perchiorate, distilled water, pnd dilute to 1 liter with isopropanol; 1.22 g of barium chioride diriydrate (BaCl-2H-2) may be used instead of the barium perchiorate, Standardize with sulfuric soid as in Section 5.2. This solution must be protected against evaporation at all times.

emorate. Standardize with summer some some section of This solution must be protected against evaporation at all times.

RULES AND REGULATIONS

all Splitting Acid Standard (2010 N). Purchase or standardies to \$\text{\texit{\texi{\text{\texi{\texi{\texict{\text{\texit{\texi{\texi{\texi{\texi{\texi{\texi{\texi{\texit{\ per businessiam and burparare

STANT

4.1.1 Present 4.1 Samplins.

4.1. Priest Proparation. Follow the procedure outlined in Method 5, Section 4.1.1; filters should be inspecied, but need not be desiccated, weighed, or identiled. If the eliment was can be considered dry, i.e., moseled. If the eliment was can be considered dry, i.e., mose-

fied. If the etiment was can be considered dry, i.a., mounture free, the siles ged need not be waighed.

1.2 Preliminary Determinations. Follow the prosedure outlined in Method 5, Section 4.1.2. Preparation of Collection Train. Follow the proredure outlined in Method 5, Section 4.1.3. (except for
the second parecraph and other obviously inappurable
parts) and use Fixure 8-1 instead of Figure 5-1. Replace
the econd paracraph with: Place 100 ml of 80 persent
isoptopanol in the first impuner. 100 ml of 3 persent
bydrogen percented in both the second and third im-

pingers: retain a portion of each resent for use as a black solution. Place about 200 g of utics get in the fourth impinger.

Note.-If moisture content is to be determined by NOTE.—If moisture contant is to be determined by impinger analysis, weigh each of the first three impurgers (pies absorbing solution) to the nearest 0.5 g and record these weights. The weight of the silica gai (or silics gaines container) must also be determined to the nearest 0.5 g and recorded.

4.14 Protest Leak-Check Procedure. Follow the besse procedure outlined in Method 5, Section 4.1.4.1, noting that the probe bester shall be adjusted to the minimum temperature required to prevent condensation, and also that vecbage such as. " * plugging the inlet to the filter holder " ° ." shall be replaced by. " * " plugging the inlet to the first impungar * ." The protest 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 Pigure 8-2. The sampling rate shall not successful 0.000 m²/min (1.0 cm) during the rm. Pariodically during the lest, observe the connecting has between the probe and first impinate for signs of condensation. If it does occur, adjust the probe beater setting meant to the minimum temperature required to prevent condensation. If on monean 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 4.16 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 out-lined in Section 6.3 of Method 5. Immediately after component changes, leat-checks are optional. If these leak-checks are done, the procedure on lined in Section 4.1.4.1 of Method 5 (with appropriate modifications)

STATIC PRESSURE DO HE (IA HE)

						AMBIENT TEMPERATURE				
LOCATION						BAROMETRIC PRESSURE				
OPERATOR						ASSUMED MOISTURE, %				
DATE						PROBE LENGTH, m (ft)				
RUN NO.					Î	NOZZLE IDENT	IFICATION NO	•		
S PMPLE BOX NO						AVERAGE CAL	IBRATED NOZ	LE DIAMETER	, cm (ia.)	
Meter box no	- The second second second second second				ĺ	PROBE HEATER	A SETTING			
—— өн △ Ретэн		L				LEAK RATE, m	3/min,(dm)			
C FACTOR									eryaniana de l'Arangai, no al 100 de l'	
PITOT TUBE COEFF	ICIENT, Cp	(045)	SCHEMATIC OF	STACK CRO	ISS SECTION	FILTER NO				
	SAMPLING	VACUUM	STACK TEMPERATURE	VELOCITY HEAD (ΔP _S),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER.	FAS SAMPLE		Temperature As meter	TEMPERATURE OF GAS LEAVING CONDENSER OR	
TRAVERSE POINT	TIME (8), paris	Em Hg	(Te). °E (°F)	810 H20 (is. H20)	метен, яни Н2О (In. Н2О)	VOLUME.	OC (OF)	00TLET, °C (°F)	LAST IMPINGER, OG (OF)	
	,									
								_		
TOTAL							Avg	Avg		
AVERAGE							Avg			

Figure 8-2. Field data.

After turning off the pump and recording the final modings at the condition 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 stail either correct the sample volume, as outlined in Section 6.3 of Method 5, or small void the run.

Drain the ice bath and, with the probe disconnected, purise the remaining part of the train, by drawing clean a visual form rate used for sampling.

Morra—Clean ambient air can be provided by passing

a wrigh now have used in sampling.

Nore.—Clean ambient air can be provided by pasting oir through a chartost diter. At the option of the tester, ambient air (without desires) may be used.

Calculation of Percent Isokinetic, Follow the rossdure outlined in Mellod S, Section 4.1.6.

42 Sumple Samprary.

4.21 Container No. 1. If a moisture content analysis

is to be done, weigh the first impinger pins contents to the nearest 0.5 g and record this weight.

Transfer the contents of the first impinger to a 2%-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 isopropanel. Add the rinse solution to the cylinder. Dilute to 25 ml with 80 percent isopropanel. 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 sud-lidentify 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 silics gel (or silica gel plusimpurer) 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 ball of filter holder) between the filter and silica gel implinger with denomized,

between the alter and silica gal impinger with desocited,

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. Beal and identify the sample container.

sample container.
4.3 Arialyms
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 notice acie 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. Share the container holding the isopropanol solution and the filter. If the filter breaks up, silow the fragments to settle for a few minutes before removing a sample. Private a 100-ril aliquot of this solution into a 250-mi Erlenmeyer flask, add 2 to 4 drops of thorn indicator, and tirate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the utilization

values. Replicate titrations must agree within 1 percent or 0.2 mi, whichever is greater.

4.3.2 Coutainer No. 2. Thoroughly mir the solution in the container holding the contents of the second and third impingers. Pipette a 10-mi silquot of sample into a 250-mi Ericomeyer flast. Add mi of isopropanol, 2 to 4 drope of thorin indicator, and titrate to a punk end point using 0.0100 N berium perchlorate. Repeat the intration with a second aliquot of sample and avarage the intration values. Replicate directions must agree within 1 percent or 0.2 mi, whichever is greater.

4.3.3 Slanks. Prepare bianks by adding 2 to 4 drope of thorin indicator to 100 mi of 80 percent isopropanol. Titrate the bianks in the same manner at the samples.

3.1 Calibrate equipment using the procedures specified in the following sections of Mathod 5: Section 3.2 (metering system); Section 5.5 (temperature gauges); Section 5.7 (baromatar). Note that the recommended leak-check of the metering system, described in Section 5.5 of histhod 5. also applies to this method.

5.2 Standardize the caritom perchlorate solution with 25 mi of standards soliture soid, to which 100 mi of 100 percent isopropanol has been added.

6. Calculations

Note.—Carry out calculations retaining at least one arms decimal frure beyond that of the acquired data. Bound off figure after final calculation.

6.1 Nomenciature.

A.= Cross-sectional area of nosile, m² (ft*).

B.= Water vapor in the gas aream, proportion by volume.

CH. 80 (= Sulfuric acid (including 50)) concentration, g/dscm (lb/dscf).

CSO₂=Sulfur dioxide concentration, g/dscm (lb/dscf). dscn.

Description of isokinstic sampling.

N=Normality of barium perchlorate dirant, g equivalents/liter.

Pha=Barometric pressure at the sampling site, mm Hg (in. Hg).

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

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

Pstd=8tandard absolute pressure, 750 mm Hg (20.92 in. Hg).

T.=Average absolute dry gas meter temperature (see Figure 8-2), ° K (° B).

T.=Average absolute stack gas temperature (see Figure 8-2), ° K (° R).

Tstd=Standard absolute temperature, 200° K (232° B).

V.=Volume of sample aliquot titrated, 100 ml (or H.SO) and 10 ml for 50 s.

Vi.=Total volume of liquid collected in impingers and silica gal, mi.

V.=Volume of gas sample as measured by dry gas meter, dem (dof).

V.(std) = Volume of gas sample measured by the dry gas meter, dem (dof).

gas meter corrected to mandard conditions, down (dscf).

**Average stack gas velocity, calculated by Method 2. Equanon 2-9, using data obtained from Method 3, mirec (tives).

Vsoin = Total voitume of solution in which the sulturic soid or sultur dioxide sample is contained, 250 miler (downloss sample is contained, 250 miler floor mile titrant used for the sample, mile **Vis=Volume of berium perchlorate fitrant used for the blank, mile **Y=Dry gas meter calibration factor.

**AH=Average pressure drop across orifice meter, mm (ii) H-0.

**6=Total sampling time, min.

**13.5=Specific gravity of mercury.

60=seconds.

**5.3 Average dry gas meter temperature and average grifice pressure drop. See data sheet (Figure 8-2).

**5.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (CO C and 750 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{\text{m (aid)}} = V_{\text{m}} Y \left(\frac{T_{\text{aid}}}{T_{\text{m}}} \right) \frac{P_{\text{bar}} + \left(\frac{\Delta H}{13.6} \right)}{P_{\text{aid}}}$$

$$=K_{i}V_{m}Y\frac{P_{bar}+(\Delta H/13.6)}{T_{m}}$$

Equation 8-1

K₁=0.3858 K/mm Hg for metric units. =17.64 R/m. 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_a in Equation 8-1 as described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volums of Water Vapor and Moisturs Content. Calculate the volume of water vapor using Equation 5-2 of Method 5: the weight of water collected in the impingers and silics get can be directly converted to multiliters (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 "Notes" in Section 6.3 of Method 5 also applies to this method. Note that if the affinent gas stream can be considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time considered dry, the volume of water vapor and more time of the considered dry, the volume of the co and mousture content need not be calculated.

6.5 Sulfurio seed mist (including 80)) concentration.

$$C_{\rm H_2 2O_6} = K_3 \frac{N(V_i - V_{\rm th}) \left(\frac{V_{\rm bein}}{V_a}\right)}{V_{\rm m \, (sub)}}$$

Equation 8-2

 $K_1=0.04904$ s/milliequivalent for metric units. =1.081 \times 10⁻¹10/med for English units. 6.6 Bullur dioxide concentration.

$$C_{5O_2} = K_2 \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{bola}}}{V_a}\right)}{V_{\text{max}(s=0)}}$$

Equation 8-3

K;=0.0000 g/maq for metric units. =7.061×10-41b/maq for English units. 6.7 Isoxinatic Variation. 6.7.1 Calculation from raw data.

$$I = \frac{100 \, T_{\bullet} [K_{\bullet} V_{1,\bullet} + (V_{\bullet} / T_{\bullet}) \, P_{bar} + \Delta H / 13.6)]}{60 \, \theta \, V_{\bullet} \, P_{\bullet} \, A_{\bullet}}$$

Equation 8-4

where:

K:=0.003484 mm Hg·m³/mi°K for metric units.

=0.002878 in. Hg·tt³/mi°R for English units.

6.7.2 Calculation from intermediate value.

$$I = \frac{T_{\bullet}V_{\text{m (std)}}P_{\bullet id} 100}{T_{\text{atd}}\sigma_{\bullet}\theta A_{\alpha}P_{\bullet} 60 (1-B_{\text{m o}})}$$

$$= \vec{K}_{\bullet} \frac{T_{\bullet}V_{\text{m (std)}}}{P_{\bullet}v_{\bullet}A_{\alpha}\theta (1-B_{\text{m o}})}$$

Equation 8-5

where: $K_s = 4.220$ for metric units. = 0.00450 for English units. 6.8 Acceptable Results. If 90 percent $\leq 1 \leq 110$ percent, the results are scooptable. 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.

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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. 91-504, 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 21pm (0.071 ±m). Continue sampling until the dry the meter remoters about 30 liters (1.1 ft) or until visible hermid droplets are carned over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings at required by Figure 4-1.

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

3.2. Calculations. The calculation method presented is designed to estimate the measure in the stack gas; therefore, other data, when are only necessary for accurate mosture desarminations, are not collected. The following equations adequately estimate the mosture content, for the purpose of determining teatment sampling rate sections.

indiving extensions acaquatery scatters in most accordent, for the purpose of determining testinetic sampling rate sections.

3.3.1 Nomenciature:

Busself approximates proportion, by volume, of water vapor in the one arream leaving the second impumper, 0.023.

Busself approximates proportion by volume.

Musself approximate presents, proportion by volume.

Musself approximate presents, proportion by volume.

(3.0 °b/h)-mole)

Pusself approximate presents, 18.0 g/g-mole (18.0 °b/h)-mole)

Pusself approximate presents, 18.0 mm Hg (29.32 ln. Hg):

[Remole] (20.5) for metter units and 21.85 (in. Hg) (m/h)-mose) (20.5) for English units.

$$V_{wq} = \frac{(V_f - V_i)\rho_w RT_{od}}{P_{odd}M_w}$$
$$= K_1^{-}(V_f - V_i)$$

Equation 4-5

K₁=0.001333 m4ml for metric units =0.04707 ft²/ml for English units.

2.3.3 Gas volume:

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

$$= K_2 \frac{V_m P_m}{T_m}$$
Equation 4-6

riere:

K:=0.1868 *K/mm Hg for metric units
=17.64 *R/m. Hg for English units

3.2.4 Approximate moisture content.

$$B_{r,s} = \frac{V_{od}}{V_{od} + V_{in (sed)}} + P_{oo}$$

$$= \frac{V_{od}}{V_{od} + V_{in (sed)}} + (0.025)$$
Equation 4-7

4. Calibration

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5. Section 5.2 (metaring system); Section 5.5 (temperature gauges); and Section 5.7 (berometer). The recommended leak check of the instruming 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 baronmeter.

8. Bibliography

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Research Triangle Parz, N.C. Publication No. AP-40, 1973.

2. Devorkin, Howard, et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Anguess, Calif. November, 1983.

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

METEOD 5-DETERMINATION OF PLRTICULATE EMISSIONS
FROM STATIONALY SOURCES

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn iso-kinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 122±14° (242±25° F) or such other tamperature 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 gravimatrically after removal of uncombined water.

1.2. Applicability. This method is applicable for the determination of particulate emissions from scatterary SOUTE OF.

... 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-08-1 (Citation 2); commercial models of this train are also available. For changes from APTD-08-1 and for allowable modelf-sations of the train shown in Figure 5-1, see the following subsections.

Figure 5-1, see the following subsections.

The operating and maintanance procedure: 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:

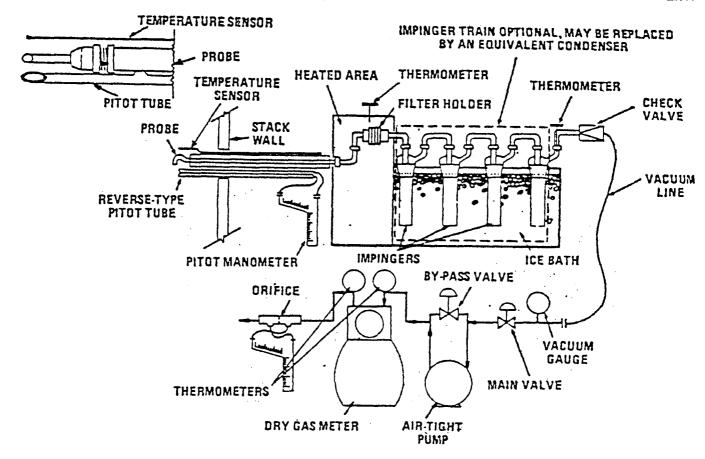


Figure 5 1. Particulate-sampling train.

2.1.1 Probe Norths. Stabaless steel (216) or gless with sharp, tapered leading edgs. The angle of taper shall be ≤30° and the taper shall be on the outside to preserve a constant internal diameter. The proble north shall be of the button-hook or elbew design, unless otherwise specified by the Administrator. If made of sminless steel, the north shall be constructed from sampless tub-

of the bottop-load or above desirt, timede of stainless specified by the Administrator. If made of stainless specified by the Administrator. If made of stainless sized, the nostle sized be constructed may be used, subject to the approval of the Administrator.

A range of nostle sizes suitable for isolcinetic sampling should be available, a.g., \$1.27 to \$1.77 cm (\$\frac{1}{2}\$ to \$\frac{1}{2}\$ in \$1.75 cm (\$\frac{1}{2}\$ to \$\frac{1}{2}\$ to \$\frac{1}{2}\$ to \$1.75 cm (\$\frac{1}{2}\$ to \$\frac{1}{2}\$ to \$\frac{

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 prob. (as shown in Figure 5-1) to allow constant monituring of the ack gas velocity. The impact (high pressure) opening

Mention o, trade names or specific product, does not estitute endorsement by the Environmental Protoc-Log Arency.

plane of the pitot tube shall be even with or above the nonzie entry plane (see Method 2. Figure 2-6b) during sampling. The Type 8 pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differentia Pressure Gauge Inclined manometer of equivalent deriva (two), as excribed in Section 2.2 of Method 2. One manometer shall be used or velocity bend (ap) readings, and the other, for ordice differential pressure readings.

pressure readings.

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

Filter Heating System. Any heating system enpable of maintaining a temperature around the filter holder during sampling o. 120±14° C (28±2° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administratory 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 APTU-0381 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 teak-tree ground glass littings or any similar leak-tree 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.) It glass tube extending to about 1.3 cm (½ in.) from the bottom of the flast. 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 class, or using flexible vacuum lines to connect the filter houder to the condenser) may be used, judget 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 stices get, or equivalent desiceant. A thermometer, expudic of measure

ing 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 coodensed and moisture leaving the condenser, each to within 1 mi or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetnessly or volumetrically and to measure the mosture leaving the coodenser by:

(1) monitoring the temperature and pressure at the exit of the coodenser and using Daiton's law of partial pressures; or (2) passing the sample gas stream through a tarted silics gel (or equivalent dedicant) trap with exit gases kept below 20° C (65° F) and determining the weight gain.

If means other than silics gel are used to determine the amount of moisture leaving the condenser, it is

If means other than siles get are used to determine the amount of moistane leaving the condenser, it is recommended that siles get (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

and to avoid the need to make corrections for mossure in the metered volume.

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

contacted as to the sample recovery and analysis of the impinger contents.

2.1.3 Metering System. Vacuum gange, leak-free pump, thermometers capable of measuring temperatum to within 2 C.5.4 P), drygas metercapobie 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 or determining sample volume 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 high role of the system shall enable o

This Barometer, Mercury, anerold, or other barometer capable of measuring atmosphene pressure to with a Chilin Hg (Cli in, Hg). In many cases, the barometric remaining 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 points shall be applied at a rice of minus 2.5 mm Hg (0.1 in, Hg) per 33 m (100 ft) rejevation increase or vice versa for elevation decrease. 2.1.10 Gas Dennity Determination Equipment, 2.1.10 Gas Dennity Determination Equipment, Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Section 2. and gas analyzer, finecessary, as described in Mathod 3. The temperature ensor shall, preferably, be permanently attached to the pitot tube or sampling or the in a fixed configuration, so that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. edge of the probe shouth 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 pisceed. 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 I percent in the average velocity measurement is to be introduced, the temperature gauss 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 Itams are

needed.
2.2.1 Probe-Liner and Probe-Nozzla Brushes. Nylon needed.

2.2.1 Probe-Liner and Probe-Norsis Brushes. Nylon busile huishes with stainless steel was handles. The probe huish shall nave extensions tat least as long as the probes of stainless steel, Nylon. Tesion, or similarly liner material. The Duishes shall be properly sized and shaned to brush out the probe liner and norzie.

2.2.2 Wash Bottles—Fivo. Glass, wash bottles are recommended, polyethysene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethysene buttles for longer than a month.

- Glass Sample Storage Containers, Chemically reastant, forosilicate glass bottles, for acctone washes, 500 pl of 1000 ml. Screw cap liners shall either be rubberbecked. Tedon or shall be constructed so as to be leak-free and resistant to chemical attack by acctone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polysthylene bottles may be usad.
- 2.2.4 Petri Dishes. For filter samples, glass or poli-ethylene, unless otherwise specified by the Admin-
- Graduated Cylinder and/or Balanca. To meas-2.25 22.5 Graduated Cyunder analor Balanca. To measure condensed water to within 1 ml or 1 g. Graduated cylindric 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.

 2.3.6 Plastic Storage Containers. Air-tight containers to torskilling call.

to store silica ael.

- to store silicages.

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

 2.2.8 Funnel, Glass or polyethlene, to aid in sample.
- recover Analysis. For analysis, the following equipment is

Glass Weighing Disbes. 2.3.1 Glass Weig 2.3.2 Desices tor

- 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 tempera-
- ture of the laboratory environment.

3. Reagents

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

follows:

3.1.1 Filters. Olass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (\$0.05 percent penetration) on 0.3-micron dioctyl phthiaste moke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2060-71. 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, II

program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, d to 16 mesh, II previously used, dry at 175° C (350° F) for 2 hours. New silics gel may be used as received. Alternatively, other types of desiceants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Water. When analysis of the material caucht in the impingers is required, distilled water shall be used. Run blanks prior to held use to eliminate a high blank.

on that samples.
3.1.4 Crushed Ice.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acctone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Afternatively, client types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Fample Recovery. Acctone-reagent grads. <0.001 percent residue, in glass bottles—is required. Acctone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acctone thanks shall be run prior to field use and only acctone with low blank values (<0.00) percent shall be used. In no case chall a blank value of greater than 0.001 the weight of Gestone used be subtracted from the stable of Gestone used be subtracted from the weight. the eather weight.

... Analysis. Two reasons are required for the analy-

3.3.1 Acetone. Same as 3.2.
3.3.2 Desicent. Anhydrous calcium sulfate, indicate
as type, Alternatively, other types of desiceants may be LOR TYPE. used, subject to the approval of the Administrator.

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 Pretent Preparation. All the components shall be maintained and chilbrated according to the procedure described in APTD-0678, unless otherwise specified berein.

Neigh several 200 to 300 g portions of silicaged in air-dight containers to the nearest 0.5 g. Record the total weight of the nicagel plus container, on each container. As an alternative, the silicagel need not be prevented, but may be weighed directly in its impinger or sampling

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 mechines 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.

glass of plante petri dishes) and keep the filters in these containers at all times emert during sampling and weighing.

Desicoate the filters at 20±5.6° C (88±10° F) and ambient pressure for at least 24 hours and weight, i.a., CO.3 mg chance from previous weighing: record results to the nessers 0.1 mg. During each weighing the filter must not be erposed to the laboratory atmosphere for a period vreater (ban 2 minutes and a relative humidity above 30 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven died at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those doscribed, 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 raminism number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temporature, and the range of velocity heads using Method 2: It is recommended that a leak-check of the pitor 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 isolinetic sampling rate settings.

using Approximation Action 4 or its alternatives in the purpose of making isosinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.5; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously and for the same total length of time as, the par ticulate 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 isoknetic sampling rates. Daring the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the more of velocity heads encountered (see Section 2.2 of Method

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

arringe 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 time temping errors.

In minute, in order to avoid time teeping 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.

these cases, the Administrator's approval must first be obtained.

41.3 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 mil of water in each of the first two unpingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel may be used, but care should be taken to ensure that it is not used, but care should be taken to ensure that it is not used, but care should be taken to ensure that it is not used. But care should be taken to ensure that it is not used in the sample recovery Alternatively, the weight of the silica gel pius 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 litter in too litter holder. Be sure that the filter is properly centered and the gasket properly paixed so as to prevent the sample gas stream from circumtivious the filter. Check the filter for tears after assembly is completed.

When glass liners are used install the selected noisile sung a Vision A O-ring when stack temperatures are less than 2-4° C 1000° F) and an ashestos string gasket when temperatures are bigher. See APTD-6076 for

details. Other connecting systems using either 316 stain less steel or Tedon ferroles may be used. When metal liners are used, install the notate 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 note. pline point

the truin as in Figure 5-1, using (I necessary) a very light cost of sulcone grasse on all ground glasses of substances of sulcone grasses of substances of substa SLOCK SAL.
Place crushed ice around the impurgers.

4.1.4 Leak-Cheek Procedures.
4.1.4 Protest Leak-Check A protest leak-check is recommended, but not required. If the tester opts to conduct the protest leak-check, the following procedure shall be used.

Aften the sampling train has been assembled, furn on and set the diter 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 connections. tion is used in assembling the probe norths to the probe liner, lead-check the train at the sampling nte by plug-ging the nortle and pulling a 300 mm Hg (15 in. Hg) VOCULIZIO.

warrum.

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, leux-check to their an during the leak-check. Instead, leux-check the train by first phisguing the index to the litter holder (cyclone, if applicable) and pulling a loo mm Hz (13 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 23 mm Hg (16 in. Hg) vacuum is idernatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 360 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate of 0.0037 m l/mm (0.02 cfm), whichever is less, are macceptable.

The following leak-check instructions for the sampling train described in APTD—1876 and APTD—1881 may be helpful. Start the pump with bypass valve fully open the coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve multithe desired vacuum is resched. 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 inlex to the probe, filter holder, or cyclone (if applicable) and unriedurely turn off the vacuum pump. This prevents the vater in the impungers from being lored backward into the filter holder and silics get from being entrained backward into the thard impunger.

4.1.4.2 Leak-Checks During Sample Run. If, during

silics gel from being entruined backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assambly or impinger) change becomes necessary, a leak-check shall be done according to the 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 orgreater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.0057 m/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 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 lerkings rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling

immediately after component changes, leak-checks

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 briber leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.3 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 litter of 120±14° C (23±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 day gas meter reading and end of each sampling time and after such leak check, and when sampling it has idented and after such leak check, and when sampling it has idented.

Take other readings required by Figure 5-2 of least once at such sample point during each time increment and sufficient readings when significant charges 120 percent variations in velocity head readings) necessitate additional in velocity head readings) necessitate additional sufficient percentages. variation in velocity Lean resouring) necessities sature tooks squatments in flow rise. Level and zero ma-numorister. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

PLANT

Clean the portholes prior to the test run to minimise the chance of sampling deposited material. To begin sampling, remove the notifie cap, verify that the fitter and probe beating systems are up to tampersture, and that the pitot tube and probe are properly positioned. Position the notifiest the first traverse point with the up pointing directly into the gas stream, immediately start the pump and adjust the flow to takkinede conditions. Nomographs are ovallable, which aid in the rapid adjust-

ment of the lackmette sampling rate without expressive ment of the labeltestic sampling rate without excessive computations. These computations are designed for the wheat the Type 8 prior time coefficient is (1.35±MCC), and the stack gas equivalent density (div molecular weight) is equal to MCC. APTD-0576 decairs the procedure for thing the noncopraphs. If C_{τ} and M_{ϕ} are outside the above stated ranges do not the the comographs unless appropriate stace (see Citation 7 in Section 7) are taken to compensate for the deviations.

AMRIENT TEMPERATURE

LOCATION OPERATOR DATE RUN NO. SAMPLE BOX NO. METER BOX NO. METER DAM C FACTOR PITOT TUBE COEFFI			204EM	ITIC OF STAC	CA CROSS SECTIO		BAROMETRIC PRESSURE ASSUMED MOISTURE, X PROBE LENGTH, m (IU) NOZZLE IDENTIFICATION NO. AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) PROBE HEATER SETTING LEAK RATE, m-)/min. (cfm) PROBE LINER MATERIAL STATIC PRESSURE, mm H ₂ (in. H ₂)			cm (ie.)
			Г		PRESSURE		FILTER NO		T	
	SAMPLING	VACUUM	STACK TEMPERATURE	VELOCITY HEAD	OIFFERENTIAL ACROSS ORIFICE METER	CAS SAMPLE		Temperature Cas leter	EII 128 HUI UES	Teleperature Up gas Leaving Condensie or
TRAVERSE POINT RESKUN	TIME (8), mia	mm Hg (in, Hg)	(T _S) •c (°ਸ	(APs).	mm ∺₂O	MOLUME	INLEE °C (°F)	001LET °C (°F)	TEMPERATURE *C (*F)	LAST IMPINGES.
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						<u> </u>			-	
								<u> </u>	 	
								· ·	 	
TOTAL						·	Avg.	Avg.		
AVERAGE							Avg			

Figure 5-2. Particulate field data.

When the stack is under significant negative pressure

When the stack is under significant negative pressure (height of impinger stam), take care to close the coarse adjust valve before inserting the probe into the stack to priver; water from backing into the filter holder. If newspary, 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 clintion of the gas stream.

Traverse the stack cross-section, as required by Method I or as specified by the Administrator, being careful not to bimp the probe nearly into the stack walls when sampling was the walls or when temporing or inserting the probe through the portholes; this insumines the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the remperature around the filter holder at the proper level; add more free and, if necessary, salt to maintain a temperature of less than 20°C 603°F) at the condensershing of outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across toe filter becomes too high, making isolanetic sampling dufficult to maintain, the filter named that another complete allier assembly isolated rather than attempting to change time filter itself. The first assembly as mediated that another complete allier assembly isolated as a member than attempting to change time filter itself, that include the summation of all filter assembly gain, has, A single train shall be used for the entire sample run, are put in cases where similatineous sampling is required in two or more different in two or more different in two or more in a rate division at any cases where equipment in two or more different in two or more different in the model of the cases where semilatineous sampling is required in two or more different in two or more different in the filter becomes to high the contract as a sample of the pour of the pour of the filter and the change of the pour of the filter and the contract and the change of the filte

In two that he same duct, or, in cases where equip-tion that he pressuates a change of trains. In all other situations, the medium of more trains with 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) impurged catches from each train shall be performed, unless identical noticle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impurged catches) and one analysis of impinged catches and one analysis of impinged catches the performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

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 gar patter reading, and conduct a post-test leak-check, as outlined in Servon

conduct a post-tast leak-check, as outlined in Servin 1.1.4.3. Also, leak-check the pitot lines as dascribed in Method 2, Section 3.1; the lines mist rass this leak-check, in order to validate the velocity head data. 4.1.6 Calculation of Percent Lowinetic, Calculation 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.

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 of all external particulate matter near the tip of the probe nowle 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 waver from the impurgers into the filter holder.

Before moving the sample train to the cleanup size, remove the probe from the sample train, wipe of the

silicone crease, 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 implification from the last implinger and cap the impringer. If a flexible line is used between the first impringer or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the implingers or condenser. After wiping of the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serim 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 lasing the simple will be minimized.

Sare a portion of the acctone used for cleanup as a blank. Take 200 ml of this acctone directly from the wash too the being used and place it in a glass sample container labeled "acctone blank."

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

Container No. 1. Carefully remove the filter from the allicone cream, and can the open outlet of the proba. Be

note any sonormal columnous. From the filter from the follows:

Conducte No. 1. Carefully remove the filter from the container. Use a pair of tweeters and for 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 gasker, by using a dry nyloo bright british and/or a sharp-edged blade. Seal the container.

Containe No. 2. Taking care to see that durt on the outside of the probe or other exterior surfaces does not get 1500 the sample, quantitatively recover particulate matter of usy condensate from the probe nowth, probe

fitting, probe liner, and front hold of the filter bodier by washing these components with acctone and placing the wash in a glass container. Distilled water may be used instead of acctone 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 accipts. Perform the acctone mass as follows: inases as follows:

Carefully remove the probe occase and clean the inside

insess as follows:

Carefully remove the probe notice and clean the inside surface by rinsing with sectione from a wash bottle and brushing with a nylon bristle brush. Brush until the accordance insee shows no visible particles, after which issue a fine-irine of the master surface with acctone.

Brush and rinse the inside parts of the Swagelak fitting with acctone in a smillar way until no visible particles remain.

Prinse the probe while situarting accrome into its uppersent to the probe while situarting accordance by tilting and maining the probe while situarting accrome into its uppersent to the probe while situarting accrome into its uppersent to the sample container. A furner typics or polyethylene) may be used to aid in transferring figured washes to the continuer. Follow the accrome ruse with a probe brush. Hold the probe in an inclined position, squart accrome into the upper and as the prince brush is being pushed with a twisting action through the probes had a sample container underneath the lower end of the probe, and cuten any acctone and particulate matter which is probe three times or mare until no verible particulation in the probe lines on visual magnetion. With ruinless steel or other made in probes, min the brush through in the above prescribed mainer at least an times since metal proops have small crevices in which particulate matter can be entrapped. Rinse the brush with accrone, and quantitatively collect these washings in the accrone and quantitatively collect these washings in the recommended that two people be used to clean the probe to minimize ample forces. Brushed above.

16 of recommended that alloints have been wiped clean the probe to minimize ample forces. Brushed clean the probe to minimize ample forces. Brushed clean for the probe accounted from containing that all foints have been wiped clean for the probes and protected from containing that all foints have been wiped clean for the probes and protected from containing that all foints have been wiped clean for the probes.

rum, keep brushes clean and protected from containing tion.

"All summing that all joints have been wiped clean of site and greese, clean the inside of the front half of the liter holder by rubbing the similaces with a gylon bristle briss and russing with accuracy. Runse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and litter holder. Carefully rinse out the glass cyclion, sise (if applicable). After all acctone weakings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acctone will not leak out when it is shipped to the laboratory. Mark the helith of the fluid level to determine whether or not leakings occurred during transport. Lebel the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silies gel to determine it it has been completely spent and make a notation of its condition. Transfer the silice gel from the fourth impinger to its original container and seal. A funnel may make it easier to poor the silice gel without spiling. A rubber powenian may be used as an aid in removing the silics gel from the impinger, it is not measure 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 limpingers as follows: Make

in the field, follow the procedure for container No. 3 in Section 4.3.
In Section 4.3.
Impinger Hader. Treat the impingers as follows: Make anotation of any color of dim 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 #0.5g 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 efficient 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.

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.

43. 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. Bestecate for 24 hours in a desiceator containing anhydrous calcium suifate. Weigh to a constant weight and report the results to the rearest 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 weightings, with no less than 6 hours of desiccation time between weighings.

Plant
Date
Run Na.
Filter No.
Amount liquid lost during transport
Acetone blank volume, mi
Acetone wash volume, mi
Acetone blank concentration, mg/mg (equation 5-4)
Acetone wash blank, mg (equation 5-5)

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg								
MOMPEN	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN						
1									
2	·		, -						
TOTAL		-							

·	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml.	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g• n	n I

^{*} CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml):

INCREASE, g = VOLUME WATER, mil

Figure 5-3. Analytical data.

Alternatively, the sampla may be oven dried at 105° C CENF 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 evan dry the sample at 105° C (CENF F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight. Container No. 3. Note the layer of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of 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 gravinetrically to ±0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiceate for 23 hours and weight to a constant weight. Report the results to the

impersiting and pressure. Desirects for 13 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 access 0.5 g using a balance. This stop may be conducted in the field.

"Actions Blank" Commer. Measure accions in this container either volumatically or gravimetrically. Transfer the accions to a tared 2.0 ml beaker and evaporate to dryness at ambient temperature and pressure. Desirects for 24 hours and weigh to a containt weight. Report the results to the nearest 0.1 mg.

Not2.—At the option of the tester, the contents of Container No. 2 as well as the accione blank container may be exponented 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 swired occasionally to maintain an even temperature. Use extreme care, as accione is highly faminable and has a low dash point.

5. Calibration.

Maintain a laboratory log of all calibrations.
5.1 Probe Nozzia. Probe nozzies shall be calibrated before their initial use in the field. Using a micrometar, measure the incide diameter of the nozzie to the nearest

0.025 mm (0.001 in.), Make three separate measuraments using different diameters each time, and obtain the average of the measuraments. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). when now numbers shau not exceed of min (0.000 in.), when now reshaped, sharpened, and recalibrated before shall be reshaped, sharpened, and recalibrated before use. Each nozzie shall be permanently and uniquely identified.

identified.

5.2 Pitot Tube. The Type 8 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-M76. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibrating 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 lank-check procedure will not detect reskares within the pump. For these cases the following leak-check procedure is suggested; make a 10-minute calibration run at 0.0005 m #min (0.02 cm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by its get the leak rate. The leak rate should not exceed 5.3 Metering System. Before its initial use in the field, to get the leak rate. The 0.00037 m /min (0.02 cfm). The leak rate should not exc

After each field use, the calibration of the metaring system shall be checked by performing three calibration runs at a single, intermediate ordine serting (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 macer 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, recambrate the meter over the full range of ordine settings, as outlined in APTD-0578.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

Nove.—If the dry gas meter coefficient values obtained before and after a test sense differ by more than 2 percent, the test sense shall be performed using whichever meter test sense shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Hester Calibration. The probe-beating system shall be calibrated before its initial use in the grade of the coefficient of the procedure outlined in APTD-0576 Probes constructed according to APTD-0586 need not be calibrated if the calibration curves in APTD-0576 are used.

be callerated it the calleration out was an accused.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stock temperature gauges. Dist thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

gas meter and condenser outure, small as calebrated appliest mercury-in-gians thermometers.

5.5 Leak Check of Sistering System Shows in Figure 5-1. This portion of the sampling train from the pump to the ortifice meter should be leak checked prior to initial uses and siter each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested to Figure 5-bi: Close the main valve on the meter but. Insert a one-bole ruober stopper with rubber tubing attached into the ortifice exhaust pips. Disconnect and vent the low side of the ortifice insult pips. Disconnect and vent the low side of the ortifice achieve the symmetry to it is in (5 to 7 in.) water column by blowing into the rubber rubing. Pinch off the tubing and observe the maneometer for one minuta. A loss of pressure on the manometer indicates a leak in the meter but issues, if present, must be corrected. be corrected.

5.7 Berometer, Calibrate against a mercury berometer.

6. Calculation.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Bound off figures after the final calculation. Other forms of the equations may be used as long at they give equivalent

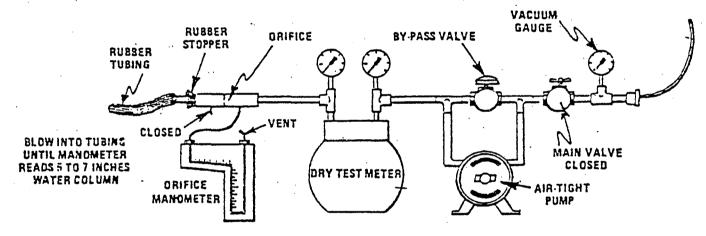


Figure 5-4. Leak check of meter box.

8.1 Nomenclature

-Cross-sectional area of nozzle, m² (lt²).
-Water Tapor in the gas stream, proportion

by volume.

- Acetone blank residue concentrations, mg/g.

- Concentration of particulate matter in stack

Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, gidsom (gidsof).
 Percent of two inetic sampling.
 Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.0067 ml/min (0.02 cm) or 4 percent of the average sampling rate, whichere is less.
 Individual leakage rate observed during the

sampling rate, whichever is less.

Individual leskar-rate observed during the leak check conducted prior to the "it" component change (i=1, 2, 3 m), mi'min (cfm).

Leakage rate observed during the post-test leak check; mi'min (cfm).

Total amount of perticulate msiter collected, mi L

L,

m.. M. -Molecular weight of water, 13.0 g/g-mole

(18.0 lb/lb-mole).

Mass of residue of acetone after evaporation. 94.

mg.

Barometric pressure at the sampling site, mm Hg (in. Hg).

Absolute stack gas pressure, mm Hg (in. Hg):

Stantard absolute pressure, 780 mm Hg (2002 in. Hg):

P = Ideal gas constant, 0.06236 mm Hg-m^{1/2} K-g-mole (21.85 in. Hg-ft-ft² R-lb-mole).

T = Absolute average dry gas meter temperature (see Figure 5-2), K (*R).

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

Standard absolute temperature, 213° K (332° R).

V = Volume of acetone blank, ml.

V = Volume of acetone used in wash, ml.

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

V = Volume of gas sample as measured by dry gas meter, dem (dcf).

V = (nd) = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V = (nd) = Volume of water vapor in the gas sample, corrected to standard conditions, sem (scf).

(sid) = Volume of water vapor in the gas sampla, corrected to standard conditions, sem (sef).

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

W.=Weight of residue in acctone wash, mg.
Y=Dry gas meter estibilation factor.
AH=Average pressure differential across the orifice meter (see Figure 5-2), mm H₂O (in. H₂O).

p.=Deusity of acctone, mg/ml (see label on bottle).
p.=Deusity of water, 0.9982 g/ml (0.02201 lb/ml).

#= Total sampling time, min.

*8:=Sampling time interval, from the beginning of a run until the first component change, min.

ArmSampling time interval, between two surcessive component changes, beginning with the interval between the first and second changes, min.

changes, min.

#, = Sampling time interval, from the first (nu) component change until the end of the sampling run, min.

13.5 = Specific gravity of marcury.

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 65° F, 29.92 in. Hg) by using Equation 5-1.

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

Equation 5-1

mi=0.3868 *Kimm He for metric units =17.64 *B/in. He for English units

Norn.—Equation 5-1 can be used as written unless the leakars rate observed during any of the mandatory leak theory (La, the post-test leak check or leak checks conducted prior to component changes) atmeds L. If L. of L. accesseds L., Equation 5-1 must be modified as follows:

(a) Case L No component changes made during sampling run. In this case, replace V a in Equation 5-1 with the expression;

$$V_{\sim} - (L_{\bullet} - L_{\bullet}) \theta$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_{-} in Equation 5-3 by the expression:

$$\begin{bmatrix} V_{\bullet} - (L_1 - L_{\bullet})\theta_1 \\ - \sum_{i=2}^{n} (L_i - L_{\bullet})\theta_{i-1} (L_p - L_{\bullet})\theta_p \end{bmatrix}$$

and substitute only for those leakage rates (L_i or L_2) which exceed L_m

5.4 Volume of water vapor.

$$V_{\text{w (and)}} = V_{1s} \left(\frac{\rho_{\text{w}}}{M_{\text{w}}}\right) \left(\frac{RT_{\text{sud}}}{P_{\text{and}}}\right) =: K_1 V_{1s}$$

where:

K;=0.001333 m²/ml for metric units

=0.04707 ftermi for English units.

6.5 Moisture Content.

$$B_{xs} = \frac{V_{x \text{ (ord)}}}{V_{x \text{ (sid)}} + V_{y \text{ (sid)}}}$$

Equation 5-3

6.10 Conversion Factors: To

or more sampling trains.

6.9 Particulate Concentration.

6.7 Acetone Wash Blank.

From Multiply by 0.02832 g/fts pr/fts 15. 43 2. 205×10⁻⁴ 33. 31 2/113

Note:—In saturated or water droplet-laden restreams, two calculations of the mouseure notion of the streams, two calculations of the mouseure notion of the stack resistant be made, one from the impunger sonaturated conditions. The lower of the two raines of $B_{\rm sub}$ shall be considered correct. The procedure for determining the notions contact based upon asymptom of saturated conditions is given in the Note of Section 1.3 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is \pm 1° C $^{\rm co}$ F), b.8. Acctone Blank Concentration.

 $C_o = \frac{m_o}{1 - c_o}$

W. = C. Vou po

Equation 3-5 6.3 Total Particulate Weight. Detarmine the total particulate catch from the sum of the weight obtained from containers 1 and 2 less the account brank 300 Figure 5-31. Note:— Relate to Section 4.1.3 to spart in calculation of results involving two or more diter assembles or two

c== (0.001 p/mg) (may V mised)

5.11 Imbinetic Variation.
6.11.1 Calculation From Raw Data.

$$I = \frac{100 \ T_{\bullet} [K_{\bullet} V_{1\bullet} + (V_{\bullet} / T_{\bullet}) \ (P_{bor} + \Delta H / 13.6)]}{60 \ \theta v_{\bullet} P_{\bullet} A_{\bullet}}$$

Entration 5-4

Equation 5-6

Pornation 5-6

R.=0.00454 mm Hg -m¹/ml - K for metric units. =0.00569 in. Hg - (t²/ml - ⁴ R for English units. 6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_{\bullet}V_{m (out)}P_{\bullet d} 100}{T_{\bullet d}r_{\bullet}\theta A_{\bullet}P_{\bullet} 60 (1-B_{v \bullet})}$$
$$= K_{\bullet} \frac{T_{\bullet}V_{m (out)}}{P_{\bullet}V_{\bullet}A_{\bullet}\theta (1-B_{v \bullet})}$$

Equation 5-8

where: $\widetilde{A} = 4.20$ for metric units = 0.00450 for English units. 6.13 Acceptable Results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable. If the results are low meaning the results are secoptable. If the results are low meaning range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make additionals. Otherwise, reject the results and repeat the test.

7. Billingraphy

7. Billiography

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Equation 5-7

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METHOD 6-DETERMINATION OF STUTE DIOXIDE EMERIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1. Principle and Applicability

1.1 Principle and Applicability

1.1 Principle and Applicability

1.1 Principle and seemple is extracted from the sampling point in the stack. The sulfure acid mist uncluding sulfur trioride) and the sulfur dioxide are separated. The sulfur dioxide traction is measured by the buruam-thorin utraction 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 50 ym (2.12×10-1 lb/ft 1). Although no upper limit has been established, that have shown that concentrations in high as \$0.000 mg/m³ of \$0, can be collected efficiently in two indeet implingers, 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 25-liter sample is about \$5,300 mg/m³.

Possible interferents are fire ammonia, waver-soluble cations, and fluorides. The caucus and fluorides are removed by glass wool filters and an isopropenol bubbler, and hence do not affect the \$0, snairys. When samples are being taken from a gas stream with high concentrations of very fine metallic himes fruch as in inlets to control devices). Is high-efficiency glass there filter must be used in pisca-of the glass wool plug (i.e., the one in the probe to remove the cation interferents.

Free summonia interferes by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate suffice and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by reacting with 50 to form particulate midite and by

redatived

2 Apparoise

FEDERAL REGISTER, VOL. 42, NO. 160-THURSDAY, AUGUST 12, 1977